J. Indian Chem. Soc., Vol LVII, No. 1, Pp. 1-112
57
[illegible] JUNE
CODEN : JICSAH LVII, (1) (1980), 1-112

JOURNAL

OF THE

INDIAN CHEMICAL SOCIETY

INDIAN CHEMICAL SOCIETY

92, ACHARYA PRAFULLA CHANDRA ROAI

CALCUTTA-700 009.

Price of Publications :

1. Catalogue of Physico-Chemical Standard Substances
Reprinted from Pure and Applied Chemistry, Vol. 29(4), 601-16 (1972)
(With the kind permission of the International Union of Pure and Applied Chemistry.)

Price : Rs. 4 (Inland, inclusive of postage)
Rs. 8 (Foreign, inclusive of postage by Surface Mail).

2. Acharya Prafulla Chandra Ray : Life and Achievements
by Prof. N. R. Dhar :

Price : Rs. 5 (Inland, inclusive of postage)
Rs. 10 (Foreign, inclusive of postage by Surface Mail).

3. Reflections on Chemical Education
by Prof. N. R. Dhar :

Price : Rs. 12.50 (Inland, inclusive of postage)
Rs. 25.00 (Foreign, inclusive of postage by Surface Mail).

4. History of Chemistry in Ancient & Medieval India
Edited by Prof. P. Ray :

Price : Rs. 30.00 (Inland, inclusive of postage)
Rs. 75.00 (Foreign, inclusive of postage by Surface Mail).

5. Abstracts of Plenary, Session & Symposium Lectures (Golden Jubilee, Indian Chemical Society, Proceedings Part I)

Price : Rs. 3.00 per copy (Inland, inclusive of postage).

6. Abstract of XX-ICCC (held at Calcutta in December 1979)

Price : Inland : Rs. 325.00 (Inclusive of Regd. Postage by Surface Mail)
Foreign : Rs. 425.00 or U. S. $ 50.00 (Inclusive of Regd. Air Mail postage)

7. Calcutta (A Tourist Guide Book)

Price : Inland : Rs. 15.00 (Inclusive of postage)
Foreign : Rs. 25.00 (Inclusive of postage by Surface Mail)

Annual Subscription (inclusive of postage) for the Journal of the Indian Chemical Society (For Non-Fellows).

For 1980

Rs. 300.00 (Inland)

Rs. 600.00 (Foreign)

Back issues of the Journal of the Indian Chemical Society and Indian Journal of Applied Chemistry (upto 1972 ; discontinued from January, 1973) may be available, for which separate enquiries are to be made for availability and rates.

I. Kar
Executive Secretary

Journal of the Indian Chemical Society

VOLUME LVII | NUMBER 1 | JANUARY 1980

CONTENTS

CONTENTS

CONTENTS

CONTENTS

INDIAN CHEMICAL SOCIETY

Journal of the Indian Chemical Society

VOLUME LVII NUMBER 2 FEBRUARY 1980

CONTENTS

CONTENTS

CONTENTS

CONTENTS

Journal of the Indian Chemical Society

OLUME LVII NUMBER 3 MARCH 1980

CONTENTS

CONTENTS

Pages

CONTENTS

CONTENTS

NOTICE

INDIAN CHEMICAL SOCIETY

The Annual Convention of Chemists 1980 will be held at the Indian Institute of Technology, Powai, Bombay during December 9-13, 1980. Information Circular & Provisional Programme may be obtained from the Office of the Indian Chemical Society, 92, Acharya Prafulla Chandra Road, Calcutta-700 009.

S. K. Talapatra

May 26, 1980

Honorary Secretary,

Indian Chemical Society,

Journal of the Indian Chemical Society

VOLUME LVII NUMBER 4 APRIL 1980

CONTENTS

CONTENTS

CONTENTS

CONTENTS

Journal of the Indian Chemical Society

VOLUME LVII NUMBER 5 MAY 1980

CONTENTS

CONTENTS

CONTENTS

CONTENTS

Journal of the Indian Chemical Society

VOLUME LVII NUMBER 6 JUNE 1980

CONTENTS

CONTENTS

CONTENTS

CONTENTS

AUTHOR INDEX

J. Indian Chem. Soc.,
Vol. LVII, January 1980, pp. 1-3

Stability Constants and Thermodynamic Parameters of Some Metal Complexes of Tridentate Schiff Base

K. K. PANDAY* and J. V. LIKHAR

Department of Chemistry, Government Science College, Gwalior (India)

Manuscript received 21 August 1979, accepted 30 November 1979

The interaction between bivalent metal ions, copper, nickel, cobalt and mercury with 3-Aldehydosalicyledene cyanoacetyl hydrazone have been studied in 70 volume per cent ethanol-water medium at different ionic strengths and at different temperatures, following the Bjerrum-Calvin pH-titration technique, as applied by Van Uitert and Haas. It is observed that all the metals form 1 : 1 complexes with 3-Aldehydosalicyledene cyanoacetyl hydrazone as established by conductance measurements also. The ligand is biprotonic. The refinement of results of stability constant were made by the method of Least-Square treatment after an algebraic transformation. The order of stability constants has been found to be Cu(II)>Ni(II)>Co(II)>Hg(II). Thermodynamic parameters for all the metallic complexes have been calculated at different temperatures and ionic strengths.

RECENTLY interest has developed in cyanoderivatives which have found their usefulness in medicine as potent drugs[1]. In several of such compounds, it has been observed that the bacteriostatic activity of the compound increases when it forms chelates with metal[2]. No work on the reaction of metals with 3-Aldehydosalicyledene cyanoacetyl hydrazone (3-ASCAH) is reported in the existing literature. The present investigations are aimed at to determine the composition and stability of the Cu(II), Ni(II), Co(II) and Hg(II) complexes with 3-ASCAH derived by the condensation of 3-Aldehydosalicylic Acid and Cyanoacetic Acid Hydrazide.

Experimental

Synthesis of Ligand :

The 3-Aldehydosalicylic acid and Cyanoacetic acid hydrazide were prepared[3,4] and taken in equimolecular proportions in alcoholic medium were made to condense after refluxing for two hours. 3-Aldehydosalicyledene cyanoacetyl hydrazone (3-ASCAH) separated as a crystalline compound. The deep yellow coloured needles of this Schiff base were purified by repeated crystallisation. The compound is soluble in alcohol and dioxane with sharp m.p. 208°.

Materials :

All reagents and chemicals used in the present work were of Analar B.D.H. grade. Pure distilled water, redistilled over alkaline permanganate and free from carbon dioxide, was used throughout the investigation. Carbonate free sodium hydroxide was prepared[5]. Perchloric acid of 0.1*M* and sodium perchlorate of 1 *M* were prepared by the dilution with water. Metal ions of requisite concentrations were prepared in double distilled water and were estimated by EDTA[6].

Apparatus :

The Elico-Conductivity Bridge Model CM-80 was used for the determination of composition of the complex with cell constant 1.09. The Metrohm *p*H meter Model E-350 A with wide range glass calomal electrode was used. Buffer solutions prepared from potassium hydrogen phthalate and borax were used for standardisation of the *p*H meter, which was done at the beginning of each titration and was checked after completion of it.

Conductometric Study :

Job's method[7] was employed to establish the composition of the complexes conductometrically. The results show that the complexes contain metal ion and ligand in the ratio 1 : 1.

Potentiometric Study :

Bjerrum-Calvin[8,9] technique modified by Irving-Rossotti[10] was employed for which the following three mixtures were prepared : (A) Perchloric acid, (B) Perchloric acid+ligand solution and (C) Perchloric acid+ligand solution+metal salt solution. The concentrations of the common ingredients were identical in different mixtures. An appropriate amount of the neutral sodium perchlorate (1 *M*) was added to maintain the desired ionic strength. These mixtures were titrated at different temperatures viz. 20°, 30° and 40° ± 0.1° against standard carbonate free NaOH (0.1 *M*), potentiometrically. Since *p*H titrations were carried out in

* Professor and Head of Chemistry Department, Government Science College, Gwalior, India.

70 volume per cent ethanol-water medium, appropriate corrections in all pH meter readings were made on account of solvent as suggested by Van Uitert *et al*[11]. A graph between pH and the volume of alkali added was plotted. The three titration curves were referred as (A) acid titration curve, (B) ligand titration curve and (C) complex titration curve.

Results

Proton-Ligand Stability Constants pK^H :

The values of $\bar{n}H$ at various pH values were calculated from the (A) acid and (B) ligand titration curves using the formula of Irving and Rossotti. Calculation of proton-ligand stability constants was carried out by plotting a graph of $\bar{n}H$ against pH extended between 0 to 2 in the $\bar{n}H$ scale. The pK_1^H and pK_2^H values corresponding to $\bar{n}H = 0.5$ and $\bar{n}H = 1.5$ respectively were obtained from the curve. However, the best value of pK_1^H of the ligand was found from the plot of log $\bar{n}H/(1-\bar{n}H)$ vs pH. This plot was found to be straight line with intercept equal to pK_1^H and slope equal to unity, suggesting that only one proton was dissociated. In the same way the value of pK_2^H was found from the plot of log $(2-\bar{n}H)/(1-\bar{n}H)$ vs pH. The values of stepwise proton-ligand stability constants obtained at various temperatures are summarized in Table 1.

TABLE 1—PROTON-LIGAND STABILITY CONSTANTS AT $\mu = 0.1M$

Temperature	pK_1^H	pK_2^H	pK^H
20°±0.1°C	10.800	4.355	15.155
30°±0.1°C	10.575	3.850	14.425
40°±0.1°C	10.405	3.205	13.610

Metal-Ligand Stability Constants :

The stepwise stability constants of the metal complexes were determined by analysing the formula curves ($\bar{n}$ versus pL). The values of $\bar{n}$, the average numbers of ligands attached per metal ion and the free ligand exponent pL were calculated from ligand and complex titration curves using the formula of Irving and Rossotti[10]. From the titration curve it is observed that the metal ligand curve is well separated from the ligand titration curves, which proves that the liberation of proton is due to chelation. $\bar{n}$ values for each system were calculated upto the pH of precipitation. After this pH second buffer region start which explain the gradual consumption of hydrogen ion by metal in formation of metal hydroxide. The values of log k_1 was obtained from the formation curves at $\bar{n} = 0.5$. The plot of $\log\left(\frac{\bar{n}}{1-\bar{n}}\right)$ against pL for the different metal systems was also drawn. From these graphical curves the values of log k_1 were evaluated.

The better values could be computed using various computational methods[12]. The constants are best evaluated by the "Least-Square Method", which makes use of all the experimental data and avoide subjective "smoothing" of data incidental to plot $\bar{n}/(\bar{n}-1)[L]$ against $(2-\bar{n})[L]/(\bar{n}-1)$ to obtain the intercept, $-K_1$ of the best straight line (1).

$$\frac{\bar{n}}{(\bar{n}-1)[L]} = \frac{(2-\bar{n})[L]}{(\bar{n}-1)} \cdot K_1K_2 - K_1 \qquad \ldots (1)$$

The values of stability constants at various temperatures and methods are summarized in Table 2.

TABLE 2—METAL-LIGAND STABILITY CONSTANTS AT $\mu = 0.1$

Metal ion	log k_1			Method*
	20°±0.1°C	30°±0.1°C	40°±0.1°C	
Copper	13.188	12.780	12.020	I
	13.295	12.886	11.987	II
	13.255	12.800	12.015	III
	13.199	12.897	11.985	IV
Nickel	11.950	11.420	10.740	I
	11.998	11.457	10.689	II
	11.962	11.437	10.737	III
	11.957	11.471	10.598	IV
Cobalt	9.512	8.955	8.265	I
	9.540	9.041	8.270	II
	9.550	8.862	8.312	III
	9.536	8.982	8.459	IV
Mercury	8.921	8.448	7.652	I
	8.941	8.463	7.602	II
	8.987	8.450	7.655	III
	8.901	8.467	7.598	IV

* I. Interpolation at half $\bar{n}$ values, II. Interpolation at various $\bar{n}$ values, III. Graphical method and IV. Least-square method.

The stability constants at zero ionic strength have also been determined from the plot of log k_1 versus $\sqrt{\mu}$ and extraploting it upto zero ionic strength Table 3.

TABLE 3—METAL-LIGAND STABILITY CONSTANTS AT VARIOUS IONIC STRENGTHS [Temp. 30±0.1°C]

Metal ion	log k_1			
	$\mu = 0.00$	$\mu = 0.02$	$\mu = 0.05$	$\mu = 0.1$
Copper	14.375	13 695	13.005	12.855
Nickel	13.075	12.455	11.705	11.500
Cobalt	10.450	9.815	8.975	8.885
Mercury	9.900	9.205	8.590	8.465

Thermodynamic Parameters :

The values of the overall changes in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) for complexes have been calculated using Gibb's Helmoltz equation[13], at different temperatures and different ionic strengths. Data for three temperatures and 0.01 ionic strength are tabulated in Table 4.

TABLE 4—THERMODYNAMIC PARAMETERS AT $\mu = 0.1$

Metal ions	Temp. in ±0.1°C	−ΔG (K.cal/mole)	ΔH (K.cal/mole)	ΔS (e.u.)
Copper	20	17.825	−13.8636	13.5201
	30	17.720		12.7278
	40	17.216		10.7105
Nickel	20	16.022	−16.9444	−3.1481
	30	15.824		−3.6646
	40	15.382		−4.9916
Cobalt	20	12.753	−19.4680	−22.9180
	30	12.416		−23.2739
	40	11.838		−24.3769
Mercury	20	11.961	−21.7857	−33.5318
	30	11.713		−33.9432
	40	10.960		−34.5869

Discussion

The result reveals that Cu(II), Ni(II), Co(II) and Hg(II) form 1 : 1 complex and the sequence of stability is found in the order : Cu(II)>Ni(II)>Co(II)>Hg(II) which is in accordance to Irving-Williams[14]. It may be mentioned here that inspite of the tendency of metal ions to hydrolyse in aqueous solution such effects have been ignored in this work as the metal chelates are stable in *p*H range studied.

The values of the stability constants reported in Table 2 are the concentration stability constants. Although the values obtained by the Least-square method would be more acceptable, it may be seen that the half integral values also are quite representative values of the stability constants. The values of log k_1 are positive in all cases and increase on decreasing the temperature, which shows that lower temperature is favourable for the formation of complexes and for their stabilities. The free energied (−ΔG) of formation of these chelates have lower values at 40° than 20° which indicates the decrease in reaction rate with increase in temperature. It is further seen that values of enthalpy change are positive in all the cases indicating the energy absorption during chelate function. The results in Table 4 show that in all systems, entropy change accompanying the formation of complexes, are positive. As a result of this the entropy term strongly favours the complex formation and accordingly chelation effect is essentially an entropy. The very large entropy change is also justified by considering the greater availability of coordination sites on these metal ions.

References

1. K. HAMNN, Ger. 703-952 (1941).
2. S. L. MUKHERJEE, J. NAHA, S. RAYMAHASAYA, S. L. LASHKAR and P. R. GUPTA, *J. Pham. & Pharmacol*, 1955, **7**, 35-38.
3. J. DUFF and E. BILLS, *J. Chem. Soc.*, 1932, 1987.
4. D. CHAKRAVARTY, A. BOSE and S. BOSE, *Pharm. Sci.*, 1964, **53**, 1086.
5. N. ALLEN and G. W. LOW, *Ind. & Engg. Chem. Anal. Edition*, 1933, **5**, 192.
6. WELCHER, The analytical uses of EDTA. Von Nostrand (1958).
7. P. JOB, *Ann. Chim.*, (Paris), 1928, **9**, 113.
8. J. BJERRUM, Metal ammine formation on aqueous solution, p. 298 Haase, Copenhagen, 1941.
9. M. CALVIN and K. W. WILSON, *J. Amer. Chem. Soc.*, 1945, **67**, 2903.
10. H. M. IRVING and H. S. ROSSOTTI, *J. Amer. Chem. Soc.*, 1954, **76**, 2904.
11. L. G. VAN UITERT and C. G. HAAS, *J. Amer. Chem. Soc.*, 1953, **75**, 451.
12. H. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.*, 1953, 3397.
13. K. B. YATSIMIRSKII and V. P. VASI'L'EV "Instability Constants of Complex Compounds", p. 63, D. VAN NOSTRAND, New York, 1960.
14. H. M. IRVING and R. J. P. WILLIAMS, *Nature*, 1948, **162**, 746.

J. Indian Chem. Soc.,
Vol. LVII, January 1980, pp. 4-5

Stepwise Stability Constants and Thermodynamic Functions of Zn(II) and Cd(II) Complexes with 2-Hydroxy-5-Chloroacetophenoneanil

Y. Z. PATHAK and G. B. JOSHI

Department of Chemistry, Saurashtra University, Bhavnagar

Manuscript received 12 September 1979, accepted 30 November 1979

The complexes of Zn(II) and Cd(II) with 2-Hydroxy-5-chloroacetophenoneanil (HCAA) have been investigated by the potentiometric titration technique in 60% v/v dioxane-water media at $\mu = 0.1M$ ($NaClO_4$). The proton-ligand stability constant and the stepwise formation constants of the complexes have been determined by the Calvin-Bjerrum pH titration technique as used by Irving and Rossotti[1]. The log K values have been determined by different methods. The overall changes in ΔG, ΔH and ΔS at 25°, 30° and 35° have also been evaluated.

THE complexes of Zn(II) and Cd(II) with (HCBA) have been studied potentiometrically[2,3]. The present investigation deals with the potentiometric studies on complexes of Zn(II) and CD(II) with 2-hydroxy-5-chloroacetophenoneanil(HCAA). The composition, stability and thermodynamic parameters like ΔG, ΔH and ΔS in 60% v/v dioxane-water media at $u = 0.1M$ at 25°, 30° and 35° have been determined.

Experimental

The expanded scale *p*H meter of systronic with a wide range (0.01 *p*H) glass electrode and a calomel reference electrode were used for *p*H measurements.

The potentiometric titration was carried out in dioxane-water 60% v/v media at constant ionic strength ($\mu = 0.1M$) maintained by adding requisite amount of sodium perchlorate solutions. The titration was carried out in an inert atmosphere. The metal perchlorate solutions were standardised complexometrically. The dioxane was purified by the method given in Vogel[4]. Carbonate free sodium hydroxide solution was prepared by a standard technique[4]. All chemicals used were of BDH AnalaR grade.

The following solutions were titrated potentiometrically against standard carbonate free sodium hydroxide (0.5 *M*) keeping the total volume of 40 ml. The temperature was maintained by immersing the cell in an electrically maintained thermostat having accuracy of ± 0.2°.

(I) 0.8 ml (1.062*M*) $HClO_4$ + 4.0 ml (1*M*) $NaClO_4$ + 11.2 ml water + 24.0 ml dioxane. (II) 0.8 ml (1.062*M*) $HClO_4$ + 4.0 ml (1*M*) $NaClO_4$ + 11.2 ml water + 2.0 ml (0.1*M*) ligand + 22.0 ml dioxane. (III) 0.8 ml (1.062*M*) $HClO_4$ + 4.0 ml (1.0*M*) $NaClO_4$ + 10.8 ml water + 2.0 ml (0.1*M*) ligand + 0.4 ml (0.1*M*) metal + 22.0 ml dioxane.

The average number of protons associated with HCAA ($\bar{n}_A$), average number of ligands attached per metal ion ($\bar{n}$) and free ligand exponent (pL) were calculated using the formulas of Irving and Rossotti[1] and the formation constants were determined by the usual computational methods as given in Table 1.

TABLE 1—STABILITY CONSTANTS OF Zn(II) AND Cd(II) CHELATES OF 2-HYDROXY-5-CHLOROACETOPHENONEANIL, AT $\mu = 0.1M$ IN 60% v/v DIOXANE-WATER MEDIA

Chelate	Temp. °C	Computational methods used		
		A	B	C
$Zn(HCAA)_2$	25	8.09 5.58 13.67	8.10 5.63 13.73	8.12 5.64 13.76
$Zn(HCAA)_2$	30	7.95 5.44 13.39	7.96 5.34 13.30	8.00 5.32 13.32
$Zn(HCAA)_2$	35	7.78 5.32 13.10	7.80 5.18 12.98	7.80 5.20 13.00
$Cd(HCAA)_2$	25	7.95 5.51 13.46	7.96 5.50 13.46	7.91 5.55 13.46
$Cd(HCAA)_2$		7.81 5.32 13.13	7.83 5.30 13.13	7.85 5.31 13.16
$Cd(HCAA)_2$	35	7.64 5.30 12.94	7.63 5.28 12.91	7.67 5.29 12.94

A = Least-square method ; B = Linear Plot method ; C = Bjerrum spreading factor method.

Results and Discussion

In the ligand it is the phenolic –OH group which takes part in the complex formation and so

the number of dissociable protons attached per ligand molecule is equal to one.

In the initial stage of the titration the ligand curve shifted to the left (or above), the acid curve due to the basic property of the tertiary nitrogen ($-C=N-$) which accepts a proton from the strongly acid medium.

The formation curve of the ligand extends over a range ($0.4<\bar{n}_A<1.9$) indicates the formation of the species HL and H_2^+L i. e., phenolic hydrogen and protonated nitrogen are completely dissociable. Log PK_1H and log PK_2H belongs to the formation of HL and H_2^+L species respectively.

The *p*H meter reading B for hydrolysis of Zn(II) and Cd(II) were around 6.4 and 7.6 respectively. The deviation of metal ligand complex titration curves were noticed around *p*H meter reading 5.2 for Zn^{2+} and 6.0 for Cd^{2+} showing the complexation of metal ion with the ligand. The values of $\bar{n}$ obtained were more than 1.0 suggesting 1 : 2 complexation.

Thermodynamic Parameters :

The values of the changes in free energy (ΔG) enthalpy (ΔH) and entropy (ΔS) accompanying the metal ligand complex forming relations have been calculated at 25°, 30° and 35° using the relations.

$$\Delta G = -RT \ln K$$

$$\frac{d\log K}{d(1/T)} = \frac{H}{4.57} \text{ (Equation of an isobaric reaction)}[6]$$

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

they are summarised in Table 2.

It is concluded that with the change in temperature there was no appreciable change in the value of stability constants or which almost remain constant.

TABLE 2—THERMODYNAMIC PARAMETERS OF Zn(II) AND Cd(II) CHELATES OF 2-HYDROXY-5-CHLOROACETOPHENONEANIL

μ=0.1*M*, Solvent : Dioxane water 60% (v/v)

$Zn(HOAA)_2$ K.cal/mole $\Delta H = -21.32$ $Zn(HOAA)_2$ e.u. $\Delta S = -10.67$

$Cd(HOAA)_2$ K.cal/mole $\Delta H = -21.61$ $Cd(HOAA)_2$ e.u. $\Delta S = -11.02$

Chelate	Temp. °C	*log β	−ΔG K.cal/mole
$Zn(HOAA)_2$	25	13.67	18.64
$Zn(HOAA)_2$	30	13.39	18.57
$Zn(HOAA)_2$	35	13.11	18.48
$Cd(HOAA)_2$	25	13.46	18.36
$Cd(HOAA)_2$	30	13.13	18.21
$Cd(HOAA)_2$	35	12.94	18.24

* Obtained from Least-square method.

The stability constant of Zn(II) complex is higher than that of Cd(II) complex.

Acknowledgement

The authors are grateful to Prof. K. A. Thaker, Head of Chemistry Department for providing necessary research facilities. We are also thankful to Saurashtra University for providing the Scholarship to one of them (Y. Z. P.).

References

1. H. Irving and H. S. Rossotti, *J. Chem. Soc.*, 1954, 2904.
2. Y. Z. Pathak and G. B. Joshi, *J. Indian Chem. Soc.*, (in press).
3. Y. Z. Pathak and G. B. Joshi, *J. Inst. of Chemists* (India), (in press).
4. A. I. Vogel, A Text Book of Practical Organic Chemistry, 3rd Edition, London, p. 177.
5. A. I. Vogel, Quantitative Inorganic Analysis, (Longman's publications, London), 1961.
6. K. B. Yatsimirskii and V. P. Vasil'Ev, "Instability Constants of Complex Compounds", p. 65, eq. no. (iii. 8).

J. Indian Chem. Soc.,
Vol. LVII, January 1980, pp. 6-10

Synthesis and Characterization of Pseudohalides of *Bis*-Methylcyclopentadienyl Titanium(IV)

V. K. JAIN, N. K. BHATIA, K. C. SHARMA and B. S. GARG*

Department of Chemistry, University of Delhi, Delhi-110 007 (India)

Manuscript received 21 September 1979, accepted 30 November 1979

The pseudohalide complexes of the (η-$CH_3C_5H_4)_2TiX_2$ type (where X=N_3, NCS, NCO and NCSe) have been prepared in aqueous medium (pH~2) as well as in non-aqueous medium. These complexes have been characterized by elemental analyses, IR and NMR spectroscopy. These complexes are monomeric in benzene solution and non-electrolytes in nitrobenzene solution. On the basis of infrared spectroscopy, it has been shown that NCS, NCO and NCSe are N-bonded to the titanium atom. Thus these are true isothiocyanato, isocyanato and isoselenocyanato derivatives. The proton chemical shifts of these complexes have also been reported.

NUMBER of organometallic pseudohalids have been reported earlier[1-5]. The two mixed halido-pseudohalido complexes of *bis*-cyclopentadienyl titanium(IV) namely $cp_2Ti(Cl)NCS$ and $cp_2TiCl(CN)$ were prepared[6] in 1963 by the reaction of cp_2TiCl_2 and AgX in toluene (where X=CNS, CN). Jansen[7] prepared $cp_2Ti(NCS)_2$ a bis pseudohalido derivative of *bis*-cyclopentadienyl titanium(IV). The complex of the cp_2ZrX_2 type (where X=CNS, CNO) were prepared[8-11] by exchange reactions from cp_2ZrCl_2 in acetone, CH_2Cl_2, C_6H_6 or nitrobenzene as follows :

$$cp_2ZrCl_2 + 2M'X \longrightarrow cp_2ZrX_2 + 2M'Cl$$

$$M' = K \text{ or } Ag$$

This paper deals with the isolation of pseudohalide complexes of the (η-$CH_3C_5H_4)_2TiX_2$ type (where X=NCS, NCO, N_3 and NCSe) from (η-$CH_3C_5H_4)_2TiCl_2$, by the reaction of sodium or potassium salts of appropriate pseudohalide in aqueous medium (pH~2) or in acetone or THF. These complexes have been identified by their elemental analyses, melting points, IR and NMR spectroscopy.

Experimental

Reagents and Techniques :

KCNS (A.R. grade, B. D. H.) and NaN_3 (A. R. grade, B.D.H.) were used as supplied. KSeCN and KCNO were prepared as cited in the literature[12]. All solvents used in the studies were properly dried. (η-$MeC_5H_4)_2TiCl_2$ was prepared by the reaction of $TiCl_4$ with $Na(CH_3C_5H_4)$ as described by Reynolds and Wilkinson[13].

Preparation of complexes in aqueous solution :

A. Preparation of (η-$CH_3C_5H_4)_2Ti(N_3)_2$:

An aqueous solution of (η-$CH_3C_5H_4)_2TiCl_2$ was made by refluxing for 30 min a 0.5 g of (η-$CH_3C_5H_4)_2TiCl_2$ in water (50 cm^3) (the pH of which was adjusted to (1.2-2) with hydrochloric acid). The clear solution so obtained was cooled to room temperature. To this aqueous solution was added an aqueous solution of NaN_3 (5 cm^3 of 10% solution) dropwise. The orange precipitates obtained were extracted with (5 × 10 cm^3) portions of CH_2Cl_2. The combined extract was dried over anhydrous $CaCl_2$ and concentrated *in vacuo* to 20 cm^3. Petroleum ether (60-80°) was added to the concentrate and the mixture was allowed to stand overnight. Bright orange crystals of the azido complex were obtained in 85% yield.

(η-$CH_3C_5H_4)_2Ti(NCS)_2$:

This complex was obtained by the method A, using (0.50 g) of (η-$CH_3C_5H_4)_2TiCl_2$ and 5 cm^3 of 10% aqueous solution of KCNS. Maroon coloured crystals of (η-$CH_3C_5H_4)_2Ti(NCS)_2$ were obtained in 70% yield.

(η-$CH_3C_5H_4)_2Ti(NCO)_2$:

This complex was obtained by the method A, using (0.50 g) of (η-$CH_3C_5H_4)_2TiCl_2$ and 4 cm^3 of 10% aqueous solution of KCNO. Red orange coloured compound was obtained in 60% yield.

(η-$CH_3C_5H_4)_2Ti(NCSe)_2$:

This complex was obtained by the method A, using (0.50 g) of (η-$CH_3C_5H_4)_2TiCl_2$ and 7 cm^3

* Author to whom correspondence should be addressed.

of 10% aqueous solution of NaSeCN. Dark-brown coloured complex was obtained in 82% yield.

Preparation of complexes in non-aqueous medium :

B. Preparation of $(\eta\text{-}CH_3C_5H_4)_2Ti(N_3)_2$:

For preparing an azido complex (1.385 g, 0.005 mol) of $(\eta-CH_3C_5H_4)_2TiCl_2$ was refluxed with (0.65 g, 0.01 mol) of NaN_3 in 200 cm^3 of tetrahydrofuran for 5 hr, filtered after cooling it to room temperature. The filtrate was concentrated to ∠0 cm^3 *in vacuo*. To the concentrated solution was added 30 cm^3 of petroleum ether (60-80°) dropwise with constant stirring. The precipitates of $(\eta-CH_3C_5H_4)_2Ti(N_3)_2$ obtained was dried *in vacuo* to give <50% yield.

$(\eta\text{-}CH_3C_5H_4)_2Ti(NCS)_2$:

This complex was obtained in quantitative yield by method B, using (1.385 g, 0.005 mol) of $(\eta\text{-}CH_3C_5H_4)_2TiCl_2$ and (0.97 g, 0.01 mol) of KCNS in 200 cm^3 acetone for 4 hr.

$(\eta\text{-}CH_3C_5H_4)_2Ti(NCO)_2$:

This complex was obtained by method B, using (1.385 g, 0.005 mol) of $(\eta\text{-}CH_3C_5H_4)_2TiCl_2$ and (0.81 g, 0.01 mol) of KCNO in 200 cm^3 THF for 5 hr. The yield was <60%.

$(\eta\text{-}CH_3C_5H_4)_2Ti(NCSe)_2$:

This complex was obtained by method B, using (1.385 g, 0.005 mol) of $(\eta\text{-}CH_3C_5H_4)_2TiCl_2$ and (1.28 g, 0.01 mol) of NaSeCN in 200 cm^3 THF for 4 hr. The yield obtained was <50%.

Physical measurements :

The IR spectra were recorded in the region 4000-250 cm^{-1} on Perkin-Elmer Model 621 grating spectrometer calibrated with polystyrene film (Table 2).

The ^1H NMR spectra were recorded on Varian A-60 spectrometer at 30° using TMS as an internal standard at a sweep width of 500 Hz. The chemical shifts are believed to be accurate to ±0.01 ppm (Table 3). The ^1H NMR spectrum for cyanato complex is shown in Figure 1.

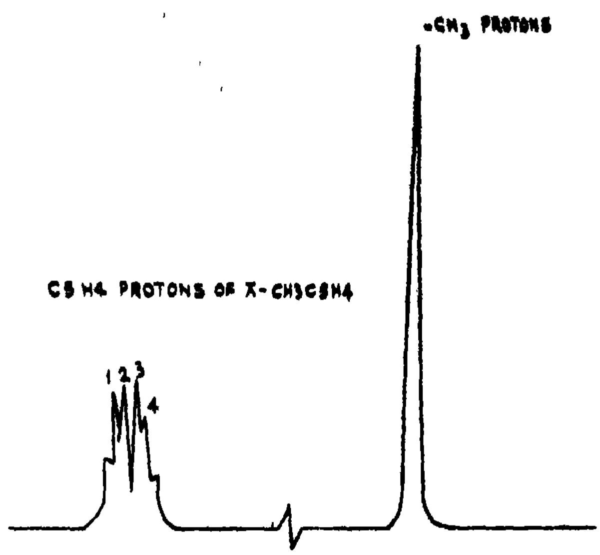


Fig. 1. ^1H NMR Spectrum of $(\eta\text{-}CH_3C_5H_4)_2Ti(NCO)_2$ at 500 cps

Conductivity measurements were made in nitrobenzene at 30±0.5° on a Beckmann RC-18A conductivity bridge. The cell constant was obtained by measuring the resistance of 0.02*M* KCl solution. C and H were got estimated microanalytically whereas Ti as TiO_2 gravimetrically. Elemental analyses, melting points, conductivity data, colours and molecular weights for these complexes are given in (Table 1).

Results and Discussion

The pseudohalide derivatives of the $(\eta\text{-}CH_3C_5H_4)_2TiX_2$ type described in this paper have

TABLE 1—ELEMENTAL ANALYSES AND CONDUCTIVITY DATA FOR PSEUDOHALIDE DERIVATIVES $(\eta\text{-}meC_5H_4)_2Ti(IV)$

Complex	Conductance data		C%	H%	Ti%	M.W.	m.p.°C and
	Λ_M ohm^{-1} cm^2 $mole^{-1}$	Molarity	Found (Calcd)	Found (Calcd)	Found (Calcd)	Found (Calcd)	colour
$(\eta\text{-}CH_3C_5H_4)_2Ti(N_3)_2$	0.64	0.5	49.6 (49.7)	4.8 (4.8)	16.3 (16.5)	350 (289.9)	113-116°(d) orange
$(\eta\text{-}CH_3C_5H_4)_2Ti(NCS)_2$	0.52	0.5	52.0 (52.2)	4.4 (4.35)	14.8 (14.9)	380 (321.9)	220-222° maroon
$(\eta\text{-}CH_3C_5H_4)_2Ti(NCO)_2$	0.62	0.5	57.5 (57.9)	4.83 (4.8)	16.35 (16.5)	300 (290)	123-126°(d) red orange
$(\eta\text{-}CH_3C_5H_4)_2Ti(NCSe)_2$	0.33	0.5	40.1 (40.4)	3.4 (3.4)	11.2 (11.5)	885 (415.9)	219-223°(d) dark-brown

TABLE 2—VIBRATIONAL FREQUENCIES OF PSEUDOHALIDE DERIVATIVES OF $(\eta\text{-meC}_5H_4)_2Ti(IV)$

$(\eta\text{-CH}_3C_5H_4)_2Ti(N_3)_2$		$(\eta\text{-CH}_3C_5H_4)_2Ti(NCS)_2$		$(\eta\text{-CH}_3C_5H_4)_2Ti(NCO)_2$		$(\eta\text{-CH}_3C_5H_4)_2Ti(NCSe)_2$	
Band (cm^{-1})	Assignment	Band (cm^{-1})	Assignment	Band (cm^{-1})	Assignment	Band (cm^{-1})	Assignment
3090m	C–H stretching of ring	3085m	C–H stretching of ring	3105m	C–H stretching of ring	3095m	C–H stretching of ring
(1442m) (1450m)	C–C (asymmetric ring breathing)	1445s	C–C (asymmetric ring breathing)	1440s	C–C (asymmetric ring breathing)	1441s	C–C (asymmetric ring breathing)
1030s	C–H (deformation in plane bending)	(1046m) (1033sh)	C–H (deformation in plane bending)	1020m	C–H (deformation in plane bending)	(1042s) (1030m)	C–H(deformation in plane bending)
840vs	C–H(bending, out of plane deformation)	848s	C–H(bending, out of plane deformation)	812s	C–H(bending, out of plane deformation)	841vs	C–H(bending, out of plane deformation)
2020vs	γ_a(NNN)	1980vs	γ(CN)	2208vs	γ_a(NCO)	2040vs	γ(CN)
1340vs	γ_s(NNN)	843s	γ(CS)	1430sh	γ_s(NCO)	700s	γ(CSe)
608sh, 600s	δ(NNN)	470m	γ(NCS)	632m, 600m	δ(NCO)	(420m) (393m)	γ(NCSe)
428sh, 405s	γ(M–N)	367s	$\gamma(CH_3C_5H_4-Ti-CH_3C_5H_4)$	390s	$\gamma(CH_3C_5H_4-Ti-CH_3C_5H_4)$	350s	$\gamma(CH_3C_5H_4-Ti-CH_3C_5H_4)$
350m	$\gamma(CH_3C_5H_4-Ti-CH_3C_5H_4)$						

TABLE 3—PROTON CHEMICAL SHIFTS (Hz) FOR PSEUDOHALIDE COMPLEXES OF $(\eta\text{-meC}_5H_4)_2Ti(IV)$

No.	Complex	Deuterochloroform solution: Ring protons $(\eta\text{-CH}_3C_5H_4)$	Deuterochloroform solution: Methyl protons $(\eta\text{-CH}_3C_5H_4)$
1.	$(\eta\text{-CH}_3C_5H_4)_2TiCl_2$	382.0, 380.2, 378 4[a]	139.3
2.	$(\eta\text{-CH}_3C_5H_4)_2Ti(N_3)_2$	372.3, 370.3, 368.0, 365.7[b]	130.6
3.	$(\eta\text{-CH}_3C_5H_4)_2Ti(NCS)_2$	384 0, 381.8, 377.0, 374.4[b]	136.5
4.	$(\eta\text{-CH}_3C_5H_4)_2Ti(NCO)_2$	377.1, 374.7, 368.0, 365.6[b]	132.1
5.	$(\eta\text{-CH}_3C_5H_4)_2Ti(NCSe)_2$	386.7, 384.2, 379.4, 377.3[b]	138.7

a = Position of three most intense peaks ;
b = Position of four most intense peaks.

been prepared from $(\eta\text{-CH}_3C_5H_4)_2TiCl_2$ by the following reaction :

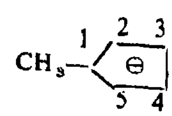
$$(\eta\text{-CH}_3C_5H_4)_2TiCl_2 + \begin{matrix}2NaX\\ \text{or}\\ 2KX\end{matrix} \rightarrow (\eta\text{-CH}_3C_5H_4)_2TiX_2 + \begin{matrix}2KCl\\ \text{or}\\ 2NaCl\end{matrix}$$

(where X = CNS, CNO, N_3, SeCN)

These complexes are soluble in organic solvent such as C_6H_6, $CHCl_3$, $(CH_3)_2CO$, CS_2 and nitrobenzene. Molecular weight determination in benzene as well as conductivity measurements in nitrobenzene indicate that these complexes are non-electrolytes and monomeric.

^1H NMR spectra :

In ^1H NMR spectra of these complexes two sharp signals in the ratio 6 : 8 are obtained i.e. (i) CH_3 protons of η methylcyclopentadienyl (ii) a multiplet due to ring protons of methylcyclopentadienyl. The ^1H NMR spectra for $CH_3C_5H_4$ group in general forwardly interpretable on the basis of 1st order spin splitting approximations. In general the CH_3 group of methylcyclopentadienyl shields both the protons of $C_{2,5}$ and $C_{3,4}$ of the substituted ring, but the effect is more pronounced for protons at $C_{2,5}$



Adjacent and crossing coupling constant ($J_{2,3}$ and $J_{2,4}$ respectively) are very nearly equal and very small than the chemical shift difference between the two pairs of protons so that a unsymmetrical triplet is obtained (as shown for $(\eta\text{-CH}_3C_5H_4)_2TiCl_2$) in Table 3, but the pseudohalide group attached to Ti is sufficiently heavy to effect further the $C_{2,5}$ and $C_{3,4}$ protons and as a combined effect of CH_3 and pseudohalide groups a multiplet showing four most intense peaks is obtained as shown in Figure 1 (a representative spectrum for cyanato complex). Similar peaks were obtained in case of other complexes.

IR spectra :

The methylcyclopentadienyl group in these complexes is identified by C–H stretching band (~ 3100 cm^{-1}), C–C (asymmetric ring breathing) (~1425 cm^{-1}), C–H (deformation in plane bending) (1125-1000 cm^{-1}) and C–H (bending out of plane deformation) at 825-800 cm^{-1}. This suggests centrally π-bonded $CH_3C_5H_4$ group in these complexes.

The azide, group in the azido complex is indicated by a characteristic asymmetric N–N–N stretching at 2020 cm^{-1} and a band at 600 cm^{-1} which is attributed to the doubly degenerate azide bending motion[14]. Other bands observed are symmetric N–N–N stretch at 1340 cm^{-1} and (Ti–N) stretch at 400 cm^{-1}. The similarity in the IR spectra with other metal azide[14] suggests an ionic bonding between Ti atom and azide group in this complex.

In the thiocyanato complex the SCN group may coordinate to the titanium atom through N or S. Mitchell and Williams[15] have shown that the C–N stretching frequencies are generally lower in M–NCS complexes than in the M–SCN complexes. The C–S stretching frequency may be used in distinguishing these two linkage isomers. For various complexes[14,16,17] involving N bonding the C–S stretching frequency is around 780-860 cm^{-1} while for the complexes involving S-bonding is around 690-720 cm^{-1}. The band at 780-860 cm^{-1} would be masked by the strong absorption at 843 cm^{-1} due to the (C-H) out of plane bending vibrations of the ring[8]. However, the absence of any band in the region 800-650 cm^{-1} together with the higher intensity of the 843 cm^{-1} band relative to 1046, 1033 cm^{-1} (C-H in plane bending) is a strong indication of the M–NCS structure in $(\eta-CH_3C_5H_4)_2Ti(NCS)_2$. Further NCS bending frequency is observed at 470 cm^{-1}.

In cyanato complex the CNO group may coordinate to titanium through O or N. So far only N-bonded complexes have been reported. For the metal cyanates (M–OC≡N), no fundamental frequency is expected around 1200-2000 cm^{-1}, while metal isocyanates (M–N=C=O) have a pseudosymmetric stretch near 1400 cm^{-1}. $(\eta-CH_3C_5H_4)_2Ti(NCO)_2$ shows one band in this region at 1430 cm^{-1} thus the complex is true isocyanato complex bonded through N.

In selenocyanato complex the SeCN group may coordinate to a metal through N or Se. The CN stretching frequencies of the Se bonded complexes are in general higher than those of the N-bonded complexes. The C–Se stretching frequency is more useful in distinguishing the type of bonding. The C–Se stretching frequency for N-bonded complexes appears at 690-620 cm^{-1} while for Se-bonded complexes around 540-510 cm^{-1} [18]. The integrated intensity of the CN stretch is also useful in the identification of N-bonded and Se-bonded complexes[19]. Burmeister and Gysling[20,21] prepared true linkage isomers [Pd(Et$_4$dien)(SeCN/NCSe)] BPh$_4$ where (Et$_4$dien=N,N,N',N' tetra-ethyldiethylenetriamine) and observed that the CN, and CSe stretching frequencies of the Se-bonded isomers are around 2123 and 532 cm^{-1} respectively whereas those of the N-bonded are around 2090 and 816 cm^{-1}. In case of $(\eta-CH_3C_5H_4)_2Ti(NCSe)_2$ complex the bands are observed at 2040 and 700 cm^{-1} respectively indicating thereby N-bonded isomer.

Acknowledgement

The authors are thankful to the Chemistry Department, University of Delhi for providing necessary facilities to carry out the present work.

References

1. J. S. THAYER and R. WEST, *Adv. Organometal Chem.*, 1967, **5**, 169.
2. R. BUNSEN, *Ann. Chem.*, 1841, **37**, 23.
3. J. S. THAYER, *Organometal Rev.*, 1966, **1**, 157.
4. M. F. LAPPERT and H. PYSZORA, *Adv. Inorg. and Radio Chem.*, 1966, **9**, 133.
5. H. N. NORBURG, *Adv. Inorg. and Radio Chem.*, 1975, **17**, 231.
6. K. L. McHUGH and J. O. SMITH, *U. S. Patent Appl.*, 1963, 3, 242, 081.
7. A. JENSEN, *Proc. Int. Conf. Coord. Chem.*, 7th, 1972, p. 25.
8. R. S. P. COUTTS and P. C. WAILES, *Aust. J. Chem.*, 1966, **19**, 2069.
9. R. S. P. COUTTS and P. C. WAILES, *Aust. J. Chem.*, 1971, **24**, 1075.
10. E. SAMUEL, *Bull. Soc. Chim. Fr.*, 1966, p. 3548.
11. J. I. BURMEISTER, E. A. DEARDORFF, A. JENSEN and V. H. CHRISTIANSEN, *Inorg. Chem.*, 1970, **9**, 58.
12. J. C. BAILER, JR (Ed), *Inorg. Synth.*, 1950, **2**, 86 and 186.
13. L. T. REYNOLDS and G. WILKINSON, *J. Inorg. Nuclear Chem.*, 1959, **9**, 86.
14. D. A. DOWS, E. WHITE and G. C. PIMENTAL, *J. Chem. Phys.*, 1959, **6**, 187.
15. P. C. H. MITCHELL and R. J. P. WILLIAMS, *J. Chem. Soc.*, 1960, 1912.
16. H. A. PAPAZIAN, *J. Chem. Phys.*, 1961, **34**, 1614.
17. S. AHRLAND, J. CHATT and N. R. DAVIES, *Quart. Rev.*, 1958, **12**, 265.

18. G. PECILE, A. TURCO and G. PIZZOLLOTO, *Ric. Sci.* 1961, **31**, 2A, 247.

19. J. L. BURMEISTER and L. E. WILLIAMS, *Inorg. Chem.*, 1966, **5**, 1113.

20. J. L. BURMEISTER and H. J. GYSLING, *Inorg. Chim. Acta*, 1967, **1**, 100.

21. J. L. BURMEISTER and H. J. GYSLING, *Chem. Commun.*, 1967, 543.

J. Indian Chem. Soc.,
Vol. LVII, January 1980, pp. 11-13

Synthesis of Some Bifunctional Tetradentate Aldimine Derivatives of Germanium(IV)

R. V. SINGH and J. P. TANDON

Department of Chemistry, University of Rajasthan, Jaipur-302 004, India

Manuscript received 28 May 1979, accepted 30 November 1979

The reactions of ethylorthogermanate with the bifunctional tetradentate aldimines derived from 2-hydroxy-1-naphthaldehyde and diamines have been studied and derivatives of the type $Ge(OC_2H_5)_2(SB)$ (where SBH_2 represents the aldimine molecule) have been isolated. The exchange reactions of these derivatives with 2-methylpentane-2,4-diol have also been carried out. The ultraviolet, infrared and proton magnetic resonance spectra of these derivatives have been recorded and their molecular weights determined ebullioscopically in chloroform. These were found to be non-electrolytes in anhydrous DMF.

A brief survey of the literature revealed extensive studies on the Schiff base complexes of transition elements and in recent years even derivatives of nontransition elements are receiving attention. Among the IV group elements, Schiff base complexes of Si(IV)[1-4], Sn(IV)[5-9] and Pb(IV)[10] have been largely investigated and the literature records only a few studies on similar derivatives of the remaining members. Reactions of ethylorthogermanate with bidentate and tridentate aldimines have been reported[11,12]. However, reactions of ethylorthogermanate with the bifunctional tetradentate aldimines do not seem to have been studied so far. The present paper reports the synthesis of germanium(IV) complexes of bifunctional tetradentate aldimines obtained by the condensation of ethylenediamine, 1,2-propylenediamine or 1,3-propylenediamine with 2-hydroxy-1-naphthaldehyde. The resulting new products have been isolated in almost quantitatively yields.

Experimental

Chemicals :

Benzene (B. D. H., A. R.) was dried by refluxing over sodium wire for several hours and finally distilled azeotropically with ethanol. Absolute alcohol was dried by refluxing over calcium oxide (anhydrous), sodium and magnesium wires respectively for several hours and finally distilled azeotropically with benzene. Ethylorthogermanate was prepared by the ammonia method[13]. It was distilled at 80°/9.0 mm before use and then analyzed :

Found : Ge, 28.69 ; OC_2H_5 ; 71.01
Calcd. for : $Ge(OC_2H_5)_4$: Ge, 28.71 ; OC_2H_5, 71.29%

The Schiff bases were prepared by the condensation of 2-hydroxy-1-naphthaldehyde with the appropriate diamine in absolute alcohol and then recrystallized.

All glass apparatus fitted with interchangeable joints was used, special precautions being taken to exclude moisture. The fractionations were carried out on a column packed with Raschig rings and fitted to a total-condensation variable take-off still head. Molecular weights were determined in boiling chloroform by means of a semi-micro ebulliometer (GallenKamp) using thermister sensing.

Analytical :

Germanium was determined as germanium dioxide and nitrogen by Kjeldahl's method. Ethanol was estimated by oxidation with normal $K_2Cr_2O_7$ in 12.5% sulphuric acid. The IR spectra were recorded in the range of 4000-200 cm^{-1} with a Perkin-Elmer 577 grating infrared spectrophotometer and PMR spectra in $CDCl_3$ on a Perkin-Elmer RB-12 spectrometer using TMS as the internal standard. The absorption spectra measurements of the solutions of aldimines and their germanium complexes in chloroform have been carried out with a Toshniwal spectrophotometer using 1 cm quartz cell in the region 600-240 nm. Conductivity measurements were carried out by conductivity bridge type 235 (ANUVIDYUT, ROORKEE) and the melting points determined in sealed tubes.

Reactions :

The reactions of ethylorthogermanate and the aldimines in 1 : 1 molar ratio were carried out in anhydrous benzene. The reaction mixture was then refluxed with the slow fractionation of ethanol-benzene azeotrope till the boiling temperature of benzene was reached and the liberated ethanol was estimated. The products were rendered free from solvent under reduced pressure and the resulting

TABLE 1—SYNTHESES, ANALYSES AND PHYSICAL PROPERTIES OF GERMANIUM COMPLEXES

$Ge(OC_2H_5)_4$ (g)	Schiff base (g)	Refluxing time (hrs)	Product, Yield (g) and characteristics	Ethanol in the Azeotrope (g) Found (Calcd.)	Analysis(%) Ge Found (Calcd.)	N Found (Calcd.)	Mol. Wt. Found (Calcd.)
1.01	$C_{16}H_{16}N_2O_2$ (1.06)	12	$Ge(OC_2H_5)_2(C_{16}H_{14}N_2O_2)$, (1.50), Yellow, solid, insoluble in benzene, melts at 271°C	0.36 (0.37)	17.00 (16.91)	6.55 (6.53)	440 (429)
0.85	$C_{11}H_{18}N_2O_2$ (0.70)	14	$Ge(OC_2H_5)_2(C_{11}H_{16}N_2O_2)$, (1.00), Brownish yellow, solid, sparingly soluble in benzene, decomposes at 220°C	0.30 (0.31)	19.49 (19.56)	7.38 (7.55)	378 (371)
1.68	$C_{11}H_{18}N_2O_2$* (1.39)	12	$Ge(OC_2H_5)_2(C_{11}H_{16}N_2O_2)$*, (2.01), yellow, foamy solid, soluble in benzene melts at 182°C	0.60 (0.61)	19.70 (19.56)	7.50 (7.55)	367 (371)

* has been used to distinguish between the compounds of the same molecular formula.

TABLE 2—SYNTHESES, ANALYSES AND PROPERTIES OF $Ge(C_6H_{12}O_2)$(SB) TYPE OF COMPLEXES

Compound (g)	$C_6H_{14}O_2$ (g)	Refluxing time (hrs)	Product, Yield (g) and characteristics	Ethanol in the azeotrope (g) Found (Calcd.)	Analysis% Ge Found (Calcd.)	N Found (Calcd.)	Mol. Wt. Found (Calcd.)
$Ge(OC_2H_5)_2(C_{16}H_{14}N_2O_2)$ (0.96)	0.26	12	$Ge(C_6H_{12}O_2)(C_{16}H_{14}N_2O_2)$, (0.95), Yellow, solid, insoluble in benzene, decomposes at 290°C	0.22 (0.21)	16.01 (15.95)	6.23 (6.15)	440 (455)
$Ge(OC_2H_5)_2(C_{11}H_{16}N_2O_2)$ (0.75)	0.23	16	$Ge(C_6H_{12}O_2)(C_{11}H_{16}N_2O_2)$, (0.66), Brown, solid, soluble in benzene, decomposes above 250°C	0.18 (0.18)	18.28 (18.26)	7.00 (7.05)	405 (397)
$Ge(OC_2H_5)_2(C_{11}H_{16}N_2O_2)$* (1.50)	0.47	15	$Ge(C_6H_{12}O_2)(C_{11}H_{16}N_2O_2)$* (1.40), Yellow, solid, soluble in benzene, melts at 245°C	0.35 (0.37)	18.35 (18.28)	7.25 (7.05)	420 (397)

derivatives were then obtained in almost quantitative yields. The experimental details of the syntheses of these derivatives are enlisted in Table 1.

Exchange reactions :

Diethoxy germanium aldimine was taken in a 100 ml R. B. Flask containing 40 ml of dry benzene and the calculated amount of 2-methylpentane-2,4-diol was added. The contents were then refluxed for 10-12 hours and the excess of the solvent was removed on the ratiohead and then under reduced pressure. The details of their syntheses, analyses and physical properties are recorded in Table 2.

Results and Discussion

The reactions of ethylorthogermanate with tetradentate aldimines (SBH_2) in 1 : 1 molar ratio can be represented as follows :

$$Ge(OC_2H_5)_4 + SBH_2 \rightarrow Ge(OC_2H_5)_2(SB) + 2C_2H_5OH$$

With a view to prepare compounds of the type $Ge(SB)_2$, 1 : 2 molar reactions were also carried out in presence of excess of aldimine, but these were found to be unsuccessful probably due to the steric factors.

The resulting compounds were obtained in the form of yellow solid and an attempt to distil some of these could not be successful. They are fairly miscible with DMF and found to be monomers in boiling chloroform. Thus the central metal atom aquires probably the coordination number six in these derivatives.

Further, the replacement reactions of $Ge(OC_2H_5)_2(SB)$ type of derivatives with 2-methylpentane-2,4-diol can be represented by the following equation :

$$Ge(OC_2H_5)_2(SB) + C_6H_{14}O_2 \rightarrow Ge(C_6H_{12}O_2)(SB) + 2C_2H_5OH$$

These are also monomeric in nature, quite soluble in chloroform and DMF and behave as non-electrolytes. However, as compared to the parent derivatives, these are quite resistant to hydrolysis and melt/decompose at higher temperatures.

Conductivity measurements :

The conductance of the newly synthesized derivatives has been determined in dimethylformamide and the results correspond to their non-electrolytic nature.

Infrared spectra :

In the case of these aldimines the stretching frequency of the hydrogen bonded OH is shifted considerably to the lower side and overlaps with the νC-H vibration exhibiting a broad band in the region 2940-2800 cm^{-1}. Freedman[14] has also reported similar absorption bands in the region 2800-2600 cm^{-1} in the spectra of N-(*o*-hydroxyphenyl)salicylideneamine and N,N′-ethylene *bis* (salicylaldimine). These bands completely disappear on chelation of the germanium to oxygen.

A band of strong intensity is observed in the 1635-1620 cm^{1} region in the spectra of Schiff bases and this may be attributed to νC=N overlapping with hydrogen bonded νC=O. However, in the germanium complexes, this is slightly shifted to the higher frequency side and this probably indicates the coordination of germanium to nitrogen[15] as well as oxygen. A strong band at around 1060 cm^{-1} may be assigned to the √Ge–O–C vibrations[16].

The maximum intensity bands in the Schiff base complexes in the regions 900-870 and 700-680 cm^{-1} are due to √Ge–O[15] and √Ge–N[17] respectively.

Proton magnetic resonance spectra :

The ^{1}HNMR spectra of N,N′-ethylene *bis* (2-hydroxy-1-naphthaldimine) and its 1 : 1 germanium complex have been recorded in $CDCl_3$. The 14.60 δ peak due to hydrogen bonded NH protons of the ligand disappears in the corresponding germanium compound indicating chelating nature of the aldimine.

The proton signal for methylene protons at 8.82δ in aldimine shifts downfield in the spectra of the germanium complex (9.35) showing their dishielding and which is possibly due to the donation of lone pair of electrons by nitrogen to the central germanium atom and resulting in the formation of a coordinate linkage. This is further supported by the fact that the signal of methine protons in the germanium complex (4.50δ) shows considerable downfield shifting as compared to the corresponding signal in the case of Schiff base (3.80δ).

Electronic spectra :

All these ligands possess three bands around 255, 320 and 405 nm. The bands around 255 nm and 320 nm respectively assigned to $\phi \rightarrow \phi^*$ and $\pi \rightarrow \pi^*$ benzenoid transitions[18], in view of the previous assignments. The remaining third band at around 405 nm is due to the $n \rightarrow \pi^*$ transition within the azomethine group. The comparison of the spectra of the complexes with those of ligands shows that there is no much change in the nature of the complexes except that the bands in the spectra of the complexes are broader and more intense than those of the aldimines.

Acknowledgement

One of the authors (RVS) is thankful to C.S.I.R., New Delhi for the award of Senior Research Fellowship.

References

1. H. Breederveld, *Rec. Trav. Chem.*, 1960, **79**, 1197.
2. H. N. Kovacs, A. D. Delman and B. B. Simms, *J. Polymer Sci.*, 1966, **4**, 1081.
3. R. V. Singh and J. P. Tandon, *J. Indian Chem. Soc.*, 1978, **55**, 764.
4. R. V. Singh and J. P. Tandon, *J. Prakt. Chem.*, 1979, **321**, 141.
5. N. S. Biradar and V. H. Kulkarni, *J. Inorg. Nuclear Chem.*, 1971, **33**, 2451.
6. V. A. Kogan, V. P. Sokolov and D. A. Osipov, *Zh. Obshch. Khim.*, 1970, **40**, 833.
7. A. V. Bergen, R. I. Cozens and K. S. Murray, *J. Chem. Soc.*, 1970, 3060.
8. K. Kawakami, M. U. Miya and I. Tanaka *J. Inorg. Nuclear Chem.*, 1971, **33**, 3773.
9. N. S. Biradar and V. H. Kulkarni, *J. Inorg. Nuclear Chem.*, 1971, **33**, 3781.
10. N. S. Biradar, V. H. Kulkarni and N. N. Sirmaradam, *Indian J. Chem.*, 1970, **8**, 838.
11. R. V. Singh and J. P. Tandon, *Synth. React. Inorg. Metal-Org., Chem.*, 1979, **9**, 121.
12. R. V. Singh and J. P. Tandon, *Monatsh. Chem.*, (In press).
13. D. C. Bradley, R. C. Mehrotra and W. Wardlaw, *J. Chem. Soc.*, 1952, 2027.
14. H. H. Freedman, *J. Amer. Chem. Soc.*, 1961, **83**, 2900.
15. V. A. Kogan, A. S. Egorov and O. A. Osipov, *Zh. Neorg. Khim.*, 1973, **18**, 2091.
16. O. Johnson and H. Fritz, *J. Amer. Chem. Soc.*, 1953, **75**, 718.
17. E. M. Belousova, I. I. Seifullina and V. N. Raznichenko, *Zh. Strukt. Khim.*, 1970, **11**, 545.
18. N. S. Biradar, V. B. Mahale and V. H. Kulkarni, *Inorg. Acta. Chim.*, 1973, **2**, 267.

J. Indian Chem. Soc.,
Vol. LVII, January 1980, pp. 14-15

Diethanolamine Complexes of Co(II), Ni(II), Zn(II) and Cd(II)

A. SAMANTRAY, S. B. MISHRA and B. K. MOHAPATRA

Department of Chemistry, Ravenshaw College, Cuttack-753 003

Manuscript received 8 August 1979, accepted 30 November 1979

Complexes of diethanolamine of the composition $[ML_2]X_2$ or $[ML_2X_2]$ have been synthesised where M = Co(II), Ni(II), Zn(II), Cd(II) and X = Cl^-, Br^-, NO_3^-, NCS^- and ClO_4^-. These have been characterised on the basis of analysis, conductance, magnetic moment, infrared and electronic spectral studies.

ETHANOLAMINES i.e. monoethanolamine, diethanolamine and triethanolamine invoke lot of interest as ligands since they contain two types of donor atoms and the hydroxy group may coordinate as such or a may be deprotonated or behave as a bridging group. . But strongly enough though a number of workers[1] have examined the behaviour of these ligands in solutions of varying pH, comparatively little attention has been paid to the solid complexes apart from a few stray reports[2-4] of their formation and stoichiometry. Hughes and Rutt have studied[5] the complexation behaviour of triethanolamine. But it has been found out from solution studies that these amines behave differently. So it was thought worthwhile to extend the investigation to the case of diethanolamine and this communication reports a number of complexes of diethanolamine with Co(II), Ni(II), Zn(II) and Cd(II) ions.

Experimental

All the chemicals used are of AnalaR grade. Ethanolic solution of metal salts were treated with diethanolamine in 1 : 2 proportion and shaken vigorously. Compounds separated out in certain cases whereas in other cases compounds were precipitated after refluxing the solution for half an hour and keeping overnight. These complexes were filtered, washed with ethanol and ether and dried in a vacuum descicator.

Metal and nitrogen were estimated by standard methods. Conductance was measured in M/1000 acetone solutions of the complexes using Toshniwal conductance bridge. Magnetic susceptibility were measured by Gouy method at room temperature (25°). Infrared spectra were recorded on KBr phase using Beckman IR –20 and IR –12 spectrophotometers. Electronic spectra were recorded in M/100 chloroform solution of complexes using Hilgerwatt uvispeck spectrophotometer. All the relevant analytical data are presented in Table 1 and spectral data in Table 2.

Results and Discussion

Diethanolamine can behave as a terdentate ligand, but in the present study it behaves as both terdentate and bidentate involving oxygen of the hydroxy group and the nitrogen of NH group. All the complexes have the composition $[ML_2]X_2$ excepting the cobalt chloride and thiocyanate complex which have the composition $[ML_2X_2]$ where L is diethanolamine and X is anion. Cobalt and nickel complexes are green in colour excepting cobalt chloride and thiocyanate complex. Zinc and cadmium complexes are white in colour. Molar conductance values of the complexes are high (Table 1) suggesting 1 : 2 electrolytic nature of the complexes and so the anions are uncoordinated, excepting the case of cobalt chloride and thiocyanate complexes where low conductance values show coordination of the anions. Magnetic moment values are in the range of 4.5-4.7, 2.9-3.2 B.M. in

TABLE 1—ANALYTICAL DATA OF COMPLEXES

Compounds	Λ_M (mhos. cm²)	μ_{eff} (B.M.)	% metal		% nitrogen	
			Found	Calcd.	Found	Calcd.
1. $[CoL_2Cl_2]$	8.5	4.9	17.05	17.34	3.85	4.11
2. $[CoL_2(NCS)_2]$	10.8	5.0	14.92	15.31	6.98	7.27
3. $[CoL_2]Br_2$	200	4.5	13.46	13.75	3.02	3.26
4. $[CoL_2](NO_3)_2$	210	4.5	15.38	15.81	7.21	7.51
5. $[CoL_2](ClO_4)_2$	280	4.7	12 28	12.59	2.68	2.99
6. $[NiL_2]Cl_2$	220	2.9	16.85	17.26	3.85	4.12
7. $[NiL_2]Br_2$	218	3.0	13.45	13.71	3.10	3.26
8. $[NiL_2](NO_3)_2$	225	2.9	14.68	14.95	6.86	7.18
9. $[NiL_2](ClO_4)_2$	240	3.1	12.25	12.55	2.64	2.99
10. $[NiL_2](NCS)_2$	215	3.2	14.85	15.26	6.88	7.28
11. $[ZnL_2]Cl_2$	220	—	18.05	18.83	7.85	8.01
12. $[ZnL_2]Br_2$	212	—	14.82	15.10	6.15	6.44
13. $[ZnL_2](NO_3)_2$	232	—	16.11	16.37	13.81	14.03
14. $[ZnL_2](NCS)_2$	216	—	16.48	16.70	14.05	14.31
15. $[ZnL_2](ClO_4)_2$	285	—	13.35	13.78	5.66	5.90
16. $[CdL_2]Cl_2$	215	—	28.54	28.98	6.84	7.12
17. $[CdL_2]Br_2$	225	—	23.43	23.64	5.45	5.80
18. $[CdL_2](NCS)_2$	220	—	25.71	25.99	12.38	12.77
19 $[CdL_2](NO_3)_2$	235	—	25.88	26.13	12.22	12.54
20. $[CdL_2](ClO_4)_2$	242	—	21.25	21.56	5.15	5.37

TABLE 2—INFRARED AND ELECTRONIC SPECTRAL DATA

Compound No.	ν(O−H)	ν(N−H)	ν(M−O)	ν(M−N)	ν_{max} in k.k. (ε)
1.	3450 3150	3300	450	355	18.8(30), 8.2(7)
2.	3450 3150	3220	455	355	19.2(32), 8.5(7)
3.	3420 3150	3300	450	360	15.5(750)
4.	3410 3150	3300	455	365	15.8(850)
5.	3420 3170	3250	450	350	16.8(810)
6.	3400	3300	455	360	23.2(14), 16.0(6), 10.2(5)
7.	3410	3250	450	355	23.5(15), 16.2(7), 10.2(6)
8.	3420	330	455	360	23.8(16), 16.5(7), 10.6(6)
9.	3410	3300	455	365	24.0(15), 16.5(6), 10.6(6)
10.	3400	3230	450	365	23.5(16), 16.5(6), 10.4(6)
11.	3390 3150	3300	425	370	
12.	3390 3160	3250	430	375	
13.	3400 3150	3300	420	370	
14.	3390 3150	3250	430	375	
15.	3450 3150	3300	425	370	
16.	3450 3170	3200	430	380	
17.	3450 3160	3300	430	380	
18.	3450 3170	3250	430	380	
19.	3390 3150	3300	435	375	
20.	3420 3160	3280	425	380	

case of cobalt(II) and nickel(II) complexes suggesting a spin free tetrahedral and octahedral configuration respectively. The pink cobalt complexes of the formula $[ML_2X_2]$ have moments in the range of 4.9-5.0 B.M. indicating a spin free octahedral stereochemistry for them.

Infrared spectra show the nitrate and perchlorate complexes to have D_{3h} and T_d symmetry of the free ions. Absorption bands were observed in the 3000-3500 cm^{-1} region due to −OH and −NH stretching vibrations. The hydroxy group absorption is less helpful than would be hoped owing to hydrogen bonding effects but Kirschner and Kiesling have distinguished[6] free and coordinated hydroxy groups in complex tartarates. In cases of all cobalt, zinc and cadmium complexes two medium intensity bands appear in the hydroxy stretching region (Table 2) suggesting possibly the presence of free and coordinated hydroxy group and splitting of the −NH band suggests coordination through the nitrogen atom. But in case of nickel complexes only one band appears in the hydroxy group stretching region indicating that both the hydroxy groups and nitrogen of the −NH group are coordinated. This has been further supported by observation[7] of ν(M−O) and ν(M−N) ~ 420-450 and 350-380 cm^{-1} region.

In the electronic spectra of cobalt(II) chloride and thiocyanate complexes two bands are observed 18.8-19.2 (30-32) and 8.2-8.5 (7) k.k. regions attributable[8] to ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ transitions respectively. A spin free octahedral configuration is presumed for these complexes being supported by the magnetic moment data. Other cobalt complexes give rise to an intense band in the 15.5-16 (800) k.k. region assignable[9] to ${}^4A_2 \rightarrow {}^4T_1(P)$ transition. The other band was probably beyond the range of instrument used. Basing on the magnetic moment values, the position and intensity of the absorption band a tetrahedral structure is suggested for these complexes. All the nickel complexes exhibit three weak absorption bands 23.2-24.0, 16.0-16.5 and 10.2-10.6 k.k. regions assigned[10] to ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g} \rightarrow {}^3T_{2g}$ transitions respectively indicating. On symmetry and hence depending on the magnetic moment and spectral data on octahedral environment is possible around the nickel(II) ion.

Basing on analytical, conductance and infrared spectral data presumably tetrahedral stereochemistry is indicated for zinc and cadmium complexes.

References

1. C. W. DAVIES and B. N. PATEL, *J. Chem. Soc. (A)*, 1968, 1824.
2. W. HEIBER and E. LEVY, *Z. anorg. allg. Chem.*, 1934, **219**, 225.
3. H. TELTAMANZI and B. CARLI, *Gazetta*, 1934, **64**, 315.
4. J. C. DUFF and E. H. STEER, *J. Chem. Soc.*, 1932, 2861.
5. M. N. HUGHES and K. J. RUTT, *J. Chem. Soc. (A)*, 1968, 2788.
6. S. KIRSCHNER and R. KEISLING, *J. Amer. Chem. Soc.*, 1968, **82**, 4174.
7. J. R. FERARO "Low Frequency Vibrations of Inorganic and Coordination Compound" Plenum Press, New York, 1971.
8. B. N. FIGGIS "Introduction to Ligand Fields", Wiley Eastern, New Delhi, 1976.
9. F. A. COTTON, D. M. L. GOODGAME and M. GOODGAME, *J. Amer. Chem. Soc.*, 1961, **83**, 4690.
10. A. B. P. LEVER "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam, 1968.

J. Indian Chem. Soc.,
Vol. LVII, January 1980, pp. 16-18

Studies on Triorthoperiodato Tetracobaltic(III) Acid, $H_3Co_4I_3O_{24}H_{12}.6H_2O$

L. C. W. BAKER

Georgetown University, Washington DC, U.S.A.

and

H. G. MUKHERJEE* and B. K. CHAUDHURI

Pure Chemistry Department, University College of Science & Technology, 92 Acharya Prafulla Chandra Road, Calcutta-700 009

Manuscript received 7 April 1979, accepted 30 November 1979

The compound $H_3Co_4I_3O_{24}H_{12}.6H_2O$ has been prepared and studies have been made on its oxidising, conductance, magnetic and semi-conducting properties.

THE compound triorthoperiodato tetracobaltic acid, $H_3Co_4I_3O_{24}H_{12}.\times H_2O$, has been prepared following known method[1] and given the composition $H_3Co_4I_3O_{24}H_{12}.6H_2O$. In this compound, the periodate ion, a strong oxidising agent, has stabilised the higher valency of cobalt(+3). This dark green polynuclear compound is a potent oxidising agent and is quite stable. As systematic studies of this compound have not yet been made, so we have studied its oxidising, acidic, conductance magnetic and semi-conducting properties.

Experimental

The compound $Na_3[Co^{III}(CO_3)_3].3H_2O$ was first prepared[2] and dissolved in appropriate amount of $HClO_4$ to which was added a known amount of sodium meta-periodate. The green crystalline product thus obtained was dissolved in hot (80°) water and crystallised from 2*M* $HClO_4$ after allowing the solution to stand for several days. After two such precipitations the crystals were collected and analysed.

Estimation :

Cobalt was estimated by the sulphate method. Iodine was analysed following the method outlined by Willard and Furman[3]. Water was determined from the weight loss at 140°. Hydrogen was estimated by Thomas CH Analyzer 35.

Found : Co = 21.13%, I = 34.09%, H_2O = 19.36%, H = 2.41% Calculated for $H_3Co_4I_3O_{24}H_{12}.6H_2O$

Co = 20.96%, I = 33.89%, H_2O = 19.22%, H = 2.40%

The polynuclear compound is dark green both in the solid state and in aqueous solution. For the determination of the oxidation state and total quantity of oxidising agents present, the following titrations were carried out :

About 0.030 gm of the compound was dissolved in about 75 ml of water, 100 ml 2(*N*) H_2SO_4 and 3 gm solid KI were added and the solution was titrated with 0.025(*N*) $Na_2S_2O_3$ solution at room temp. using starch as an indicator. It required 27.85 equivalents of sodium thiosulphate to titrate the liberated iodine per mole of the sample corresponding to the reduction of Co(III) to Co(II) and of periodate to iodine[4].

Reaction : $$[Co_4I_3O_{24}H_{12}]^{3-} + 25I^- + 36H^+ = 4Co^{+2} + 14I_2 + 24H_2O$$

In another operation, 0.0283 gm of the compound was dissolved in 60 ml water, 0.15 gm KCN was added. Then 5 ml formalin, 60 ml 2(*N*)H_2SO_4 and about 3 gm solid KI were added and the liberated iodine was titrated with 1.05 (*N*/40) $Na_2S_2O_3$ solution at room temperature to the starch-iodide end point. It required 23.90 equivalents of sodium thiosulphate solution per mole of the compound corresponding to the reduction of per-iodate to iodine.

Reaction : $$[Co_4I_3O_{24}H_{12}]^{3-} + 24CN^- = 3IO_4^- + 4Co(CN)_6^{3-} + 12OH^-$$

$$HCHO + CN^-(excess) + H_2O = CH_2(OH)CN + OH^-$$

$$3IO_4^- + 21I^- + 24H^+ = 12I_2 + 12H_2O$$

Titration was also carried out following that of Lister and Yoshino[4]. 0.0523 gm of the compound was dissolved in 50 ml water ; 50 ml 2(*N*)H_2SO_4, 25 ml 1.02 (*M*/40) Mohr solution in 1(*N*)H_2SO_4 was

* For correspondence.

added and then titrated back at room temperature with 1.025 (*N*/40) $K_2Cr_2O_7$ solution using Barium diphenylamine sulphonate as indicator. 9.93 moles of Fe^{++} were required per mole of the compound corresponding to the reduction of Co(III) to Co(II) and of periodate to iodate.

Reaction : $[Co_4I_3O_{24}H_{12}]^{3-}+10Fe^{+2}+18H^+ = 4Co^{+2}+3IO_3^-+10Fe^{+3}+15H_2O$

All these show cobalt is present in the trivalent and iodine in the heptavalent state.

Potentiometric Titration :

The acid was titrated with ferrous sulphate in acid solution potentiometrically. The cell used was $Pt/H_3Co_4I_3O_{24}H_{12}.6H_2O$ in $1(N)$ H_2SO_4/Hg_2Cl_2 in saturated KCl/Hg. The results given below are the voltages relative to the calomel (satd.) electrode.

Titration was carried out with $2.64\times10^{-4}(M)$ $H_3Co_4I_3O_{24}H_{12}.6H_2O$ in $1.0(N)$ H_2SO_4 against $0.0214(M)$ Mohr's salt at 29.5°. E.m.f. shown are in millivolts. Volume of Mohr added in ml and their corresponding change in e.m.f. are shown in parentheses. 0 ml (109.5), 0.25 ml (110.0), 0.50 (111.5), 0.75(111.8), 1.0(113.0), 1.50(114.0), 2.0(115.0), 2.5 (118.3), 3.0(125.5), 3.5(130.2), 4.0(140), 4.2(145.1), 4.4(150), 4.6(180.3), 4.8(220.2), 4.9(275.1), 5.0(335.0), 5.20(350), 5.40(365), 5.50(375), 6.0(385.6) 7.0(390), 7.5(405), 8.0(410), 8.5(420).

This shows that the compound is reduced at one step acting as a complexion, so that there is only one inflection point. The potential where the compound is full neutralised is 280 m. volt and the half-neutralisation voltage is 118 (mv), corresponding to apparent standard electrode potential relative to calomel, which may not be the true equilibrium potential. A reaction of this sort involving transfer of oxygen may well be a slow reaction, evident from the fact that the system attains equilibrium very slowly. The whole system is reduced in one step, so that we get the average standard reduction potential value corresponding to the reduction of Co^{+3} to Co^{+2} and of IO_4^- to IO_3^- species simultaneously[4].

However, the number of molecules of Mohr salt reacting is quite definite. The inflection occurs at ·10 molecules per molecule of the periodate species. This is what is required by the equation.

Reaction : $H_3Co_4I_3O_{24}H_{12}+9H_2SO_4+10FeSO_4 \rightarrow 4CoSO_4+5Fe_2(SO_4)_3+3HIO_3+15H_2O$

Conductometric Titration :

Titration of a $8.2\times10^{-4}(M)$ solution of the acid with standard $0.03(M)$ NaOH solution in a Philips conductance bridge showed two breaks—one very sharp and the other weak corresponding to the neutralisation of two protons. The third dissociation being very weak could not be followed conductometrically.

pH Titration with Standard Sodium Hydroxide Solution :

For this titration $1.53\times10^{-3}(M)$ solution of the above polynuclear acid was prepared and titrated with standard caustic soda solution in an ELICO *p*H-meter using $2(M)$ $NaNO_3$ bridge with glass electrode of 0-13 *p*H range. From the data, $\Delta pH/\Delta v$ values were calculated and plotted against 'v'-the volume of alkali.

Conductance Measurement :

Conductometric measurements in aqueous solution were carried out in a Philips conductance bridge. The results are shown in Table 1.

TABLE 1—CONDUCTOMETRIC MEASUREMENT Temp. 28°C

Dilutions in litres per mole	*p*H of the solution	Resistance (ohms)	Molar conductivity (mho – cm²)
500	2 20	0.08×10^4	674
750	2.41	0.11×10^4	736.4
1000	2.52	0.135×10^4	792
1500	2.63	0.190×10^4	840
2000	2.80	0.23×10^4	923.2

From the results it appears that the conductivity value increases gradually with dilution. The acid behaves as a weak electrolyte. The abnormally high value of molar conductance at 1024 dilution cannot be explained for a compound of this type which should ionise as $H_3A \rightleftharpoons 3H^+ + A^{3-}$ and give evidence for four ions in the solution. The molecule may contain some labile ions which is responsible to give high conductance value.

Magnetic Measurement :

Magnetic susceptibility measurement of the solid compound was carried out in a Guoy magnetic balance. The compound is slightly paramagnetic and molar susceptibility value has been found to be 137.7×10^{-6} at 20°. The pure compound would have been diamagnetic. This residual paramagnetism may arise due to the presence of some cobaltous ion in the compound.

Study of Semi-Conducting Property :

Semi-conducting property of the acid $H_3[Co_4 \cdot I_3O_{24}H_{12}]$. $6H_2O$ was studied employing sandwich cell technique with stainless steel and conducting glass electrode. Current was measured in an Electrometer Amplifier—EA 815 of E.C.I.L. (India). Heating rate 30V variac in the range 20° to 50°.

The results show that the compound possesses semi-conducting property with low activation energy of 0.16615 ev. The compound of course conducts high current. The discrepancy between high current and such low activation energy cannot however be explained from this study. It may be due to the presence of some impurity in the form of Co^{2+} ions in the original compound, which facilitates the electron transfer from valence band to conduction band. Results are shown in Table 2.

TABLE 2

Temp. (°C)	1000/T°K	Current (amp.)
22.25	3.386	8.9×10^{-7}
23.45	3.373	9.7×10^{-7}
25.50	3.35	1.09×10^{-6}
30.45	3.295	1.45×10^{-6}
32.80	3.270	1.67×10^{-6}
35.20	3.244	1.91×10^{-6}
37.50	3.22	2.20×10^{-6}
41.00	3.184	2.66×10^{-6}
43.3	3.161	3.10×10^{-6}
46.9	3.125	3.74×10^{-6}
49.3	3.102	4.20×10^{-6}

Results and Discussion

Although the acid has earlier been given the composition $H_3Co_4I_3O_{24}H_{12}.3H_2O$, our study shows it to be $H_3Co_4I_3O_{24}H_{12}.6H_2O$. It is a dark green crystalline compound which retains its green colour in aqueous solution. It possess both acidic and oxidising properties. The acid is a weak tribasic one although conductometric titration can reveal the presence of only two protons. The compound can be reduced by various reducing agents. The presence of Co(III) and I(VII) can be demonstrated from its oxidising behaviour. The reduction product depends upon the reducing agent chosen. It is stable both in the solid state and in solution. Oxidising agent with such high molecular weight (formula weight is 1124) can be used as a primary standard in analytical chemistry. The end point is sharp and colourless. The compound is reduced in one step. The polynuclear acid contains some cobaltous ion—which has been reflected in its oxidising, magnetic and semi-conducting properties. The conductance behaviour is rather abnormal.

Acknowledgement

The authors acknowledge the help of Dr. T. N. Mishra, Department of Optics, Indian Association for the Cultivation of Science, Calcutta for recording the semi-conducting data. One of the authors (B. K. C.) is recipient of grant from U. G. C.

References

1. 'Inorganic Synthesis' McGraw-Hill Book Company, Inc., 1967, Vol. 9, p. 142.
2. 'Inorganic Synthesis', McGraw-Hill Book Company, Inc., 1966, Vol. 8, p. 202.
3. H. H. WILLARD and N. H. FURMAN, 'Elementary Quantitative Analysis', 3rd Ed., D. Van Nostrand Co. Inc., New York, 1940, p. 320.
4. M. W. LISTER and Y. YOSHINO, *Canad. J. Chem.*, 1960, **38**, 45.

J. Indian Chem. Soc.,
Vol. LVII, January 1980, pp. 19-20

Polarographic Study of Zn(II)—Thiocyanate System

(Km.) KRISHNA, S. K. JHA and MUKHTAR SINGH

Chemical Laboratories, Agra College, Agra

Manuscript received 26 March 1979, accepted 30 November 1979

Polarographic behaviour of Zn(II) in the presence of increasing [thiocyanate] has been studied at a constant ionic strength $\mu=2$ ($NaNO_3$). The reduction has been found to be diffusion controlled and quasi-reversible $E_{1/2}$ of Zn(II) gets shifted to more negative potentials with increasing [thiocyanate] thereby showing complex formation. The reversible half-wave potential, ($E^r_{1/2}$) and the kinetic parameters of the electrode process have been evaluated by Gellings method. Zn(II) forms three successive complexes : $[Zn(CNS)]^+$, $[Zn(CNS)_2]$ and $[Zn(CNS)_3]^-$ and not four as reported by earlier workers[1]. Stability constants of the three complexes are $\beta_1=3$, $\beta_2=4$ and $\beta_3=10$. The percentage distribution of Zn(II) in its various forms as a function of ligand concentration has also been presented.

FRANK and Hume[1] have studied polarographically the Zn(II)-thiocyanate system at a constant ionic strength $\mu=2$ and have reported the formation of four successive complex species with stability constant $\beta_1=3\pm0.5$, $\beta_2=7\pm3$, $\beta_3=1\pm1$ and $\beta_4=20\pm2$. A perusal of these values, however, shows that the formation of third successive complex species viz., $[Zn(CNS)_3]^{1-}$ with $\beta_3=1\pm1$ is doubtful as a value of $\beta=1$ signifies the stability constant of the "zero complex"[2]. It seems, primafacie, that Zn(II) forms only three successive complexes. It was therefore thought worthwhile to verify the results of Frank and Hume. Apart from this, the nature of electrode reaction of Zn(II) in the presence of increasing thiocyanate concentration has also been ascertained and the kinetic parameters of the electrode reaction have been determined.

Experimental

All the chemicals used were of AR, BDH or E. Merck G. R. grade and their solutions were prepared in conductivity water by standard analytical procedures. $NaNO_3$ solution was used to keep the ionic strength constant ($\mu=2$). KCNS solution was used as ligand. The concentration of Zn(II) in each case was kept $1\times10^{-3}M$.

A manual polarograph in conjunction with Toshniwal Polyflex galvanometer (PL – 50) was used. All the measurements were made at $25\pm0.1^\circ$. Purified nitrogen gas was passed through the solution to deaerate it. Saturated Calomel Electrode (S. C. E.) was used as a reference electrode. The d.m.e. had the following characteristics (in $0.1M$ $NaNO_3$, open circuit). $m=2.459$ mg/sec ; $t=2.44$ sec ; $m^{2/3}t^{1/6}=2.11$ $mg^{2/3}$ $sec^{-1/2}$; $h_{corr}=61.79$ cm.

The number of electrons (n) involved in the reduction process was determined by millicoulometric method by DeVries and Kroon[3] using a mercury pool cathode. This gave the value of $n=2$.

Results and Discussion

A series of polarograms were obtained with different concentrations of ligand. The thiocyanate concentration was varied from 0 to $2M$. In each case a single well defined diffusion controlled wave appeared. The plots of i_d vs $\sqrt{h_{corr}}$ were found to be linear passing through origin indicating that the reduction is diffusion controlled. The plots of log i/i_d-i vs $E_{d.e.}$ were found to be linear with slope of the order of 40 ± 2 mV showing the quasi-reversible nature of electrode reaction[4,5].

The reversible half-wave potential has been calculated by Gellings[6] method. DeFord and Humes[7] method modified by Irving[8] has been

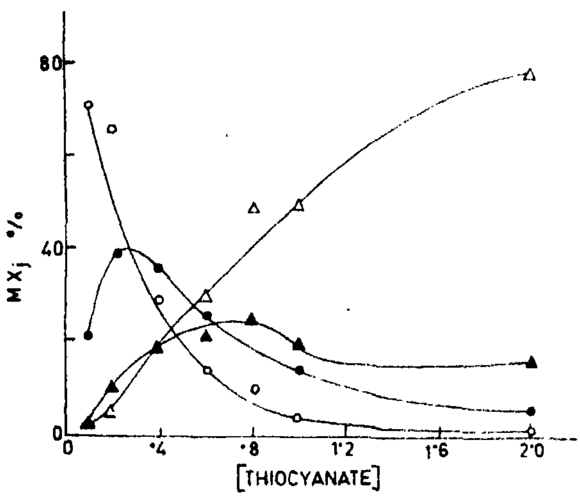


Fig. 1. Percentage distribution of Zn(II) in its various forms as a function of [thiocyanate]

O→Zn^{2+}
●→$[Zn(CNS)]^+$
▲→$[Zn(CNS)_2]$
△→$[Zn(CNS)_3]^-$

applied to determine the composition and stability constants of the successive complexes (Table 2).

TABLE 1—POLAROGRAPHIC CHARACTERISTICS OF Zn(II)-THIOCYANATE SYSTEM, $\mu = 2$

[Thiocyanate] M	$-E_{1/2}$ V (S.C.E.)	$-E'_{1/2}$ V (S.C.E.)	α	$k_{s,h} \times 10^3$ cm/sec
0	0.985	0.970	0.997	1.08
0.1	0.990	0.975	0.704	1.414
0.2	0.995	0.975	0.645	1.818
0.4	1.000	0.986	0.645	1.745
0.6	1.010	0.995	0.607	1.883
0.8	1.030	1.010	0.704	1.658
2.0	1.050	1.030	0.645	0.707

TABLE 2—VALUES OF F_j [X] FUNCTIONS AT DIFFERENT CONCENTRATIONS OF THIOCYANATE

[Thiocyanate] M	$F_0[X]$	$F_1[X]$	$F_2[X]$	$F_3[X]$
0	—	—	—	—
0.1	1.490	4.20	—	—
0.2	1.521	2.60	—	—
0.4	3.442	6.03	7.575	8.937
0.6	7.086	10.143	11.905	13.175
0.8	10.420	11.775	10.968	—
1.0	20.700	19.700	16.700	12.700
2.0	103.800	51.150	24.070	10.035

$\beta_1 = 3$; $\beta_2 = 4$; $\beta_3 = 10$.

The stability constants for three complexes: $[Zn(CNS)]^+$, $[Zn(CNS)_2]$ and $[Zn(CNS)_3]^-$ are $\beta_1 = 3$, $\beta_2 = 4$ and $\beta_3 = 10$. Fig. 1 represents the percentage distribution of Zn(II) in its various forms as a function of $[CNS^-]$.

The kinetic parameters (α and $k_{s,h}$) of electrode reaction of Zn(II)-thiocyanate system has been calculated by Gellings method and are listed in Table 1. The value of $k_{s,h}$ is of the order of 2×10^{-3} cm/sec showing[9-11] the quasi-reversible nature of the electrode process.

Acknowledgement

Thanks are due to the Principal, Dr. S. N. Srivastava, Agra College, Agra for providing *necessary facilities*.

References

1. RICHARD, E. FRANK and DAVID N. HUME, *J. Amer. Chem. Soc.*, 1953, **75**, 1736.
2. D. R. CROW, "Polarography of Metal Complexes" Academic Press, New York, 1969, p. 66.
3. T. DEVRIES and J. L. KROON, *J. Amer. Chem. Soc.*, 1953, **75**, 2484.
4. J. N. GAUR, D. S. JAIN and A. KUMAR, *Indian J. Chem.*, 1965, **13**, 165.
5. P. S. VERMA, D. S. JAIN and J. N. GAUR, *Indian J. Chem.*, 1965, **13**, 586.
6. P. J. GELLINGS. *Z. Elektrochem, Ber. Bunsenges, Phys. Chem.*, 1962, **66**, 477, 481, 799 ; 1963, **67**, 167.
7. D. D. DEFORD and D. N. HUME, *J. Amer. Chem. Soc.*, 1951, **73**, 5321.
8. H. IRVING, "Advances in Polarography". (Ed. I. S. Longmuir) Vol. I, p. 42 (Pergamon Press, London) 1960.
9. P. DELAHAY, *J. Amer. Chem. Soc.*, 1953, **75**, 1430.
10. H. MATSUDA and Y. AYABE, *Z. Electrochim.*, 1959, **63**, 1164.
11. J. KORYTA, *Electrochim. Acta*, 1962, **6**, 67.

J. Indian Chem. Soc.,
Vol. LVII, January 1980, pp. 21-22

Polarographic Studies on the Influence of the Concentration and Nature of Different Supporting Electrolytes on the Kinetics of the Electrode Process of Mn(II)

SUDHINDRA SWARUP SHARMA AND MUKHTAR SINGH

Chemistry Department, Agra College, Agra

Manuscript received 25 January 1977, revised 17 August 1977, accepted 30 November 1979

The polarographic behaviour of Mn(II) has been studied in a variety of supporting electrolytes of varying concentrations (0.05 to 1 *M*) viz., NaCl, $NaClO_4$, $NaNO_3$, KCl, $KClO_4$, KNO_3, KNO_2, KBr, KI, KH_2PO_4, pot. acetate, pot. tartrate, pot. citrate, pot. benzoate, NH_4Cl, NH_4NO_3, NHCNS, $Mg(NO_3)_2$, $Ca(NO_3)_2$, $Sr(NO_3)_2$ and $Ba(NO_3)_2$. It has been found that the reduction of Mn(II) at d.m.e. is quasi-reversible and diffusion controlled in all supporting electrolytes. The kinetic parameters, viz., the transfer coefficient (α) and standard rate constant ($k_{s,h}$), of the quasi-reversible electrode process have been calculated by Gellings' method. The influence of the concentration and nature of supporting electrolytes on the kinetics of quasi-reversible electrode process of Mn(II) has been discussed in terms of the values of $k_{s,h}$ and 'α'.

A survey of literature[1-6] reveals that the polarographic studies on Mn(II) still remain incomprehensive in as much as that no attempt seems to have been made with regard to the influence of the concentration and nature of a variety of supporting electrolytes on the kinetics of the electrode process of Mn(II) at d.m.e. With this aim in view the present study has been undertaken.

Experimental

All the chemicals used were either of A.R., B.D.H. or E.Merck, G.R. grade. Solutions were prepared in conductivity water. The resultant concentration of Mn(II) was maintained at 1.0×10^{-3} *M* in each case.

The experiments were carried out in a similar manner as described elsewhere[6]. However, a different capillary being used the d.m.e. had the following characteristics :

$h_{corr} = 61.30$ cm ; $m = 2.075$ mg/sec. ; $t = 3.45$ sec. (in 0.1 *M* KCl, open circuit) ; $m^{2/3}t^{1/6} = 2.005$ $mg^{2/3}sec^{-1/2}$.

Results and Discussion

(*i*) Mn(II) gives a single well defined wave in the majority of supporting electrolytes used. However, in some supporting electrolytes viz., $NaNO_3$, KH_2PO_4, $Mg(NO_3)_2$, $Ca(NO_3)_2$, $Sr(NO_3)_2$ and $Ba(NO_3)_2$ the waves become drawn out at higher concentration of these supporting electrolytes. The limiting current is diffusion controlled in each case as evidenced by the linearity of i_d vs $\sqrt{h}$ plots. The plots of $E_{d.e.}$ vs log $i/i_d - i$ are linear in all the cases.

(ii) On applying different criteria[7,8] of reversibility and irreversibility of the electrode process it has been found that the reduction of Mn(II) is neither totally irreversible nor does it fulfil the requirements of reversibility. The slope values of log plots lie in the range 0.040 V-0.050 V. These slope values suggest the quasi-reversible nature of the electrode process of Mn(II).

Gellings' method[9] has been used to evaluate $E^r_{1/2}$ (the reversible half-wave potential) and the kinetic parameters ('α' and $k_{s,h}$) of the quasi-reversible electrode process.

The calculated values of $k_{s,h}$ are of the same order of magnitude as suggested by Delahay[10] for quasi-reversible electrode processes.

(*iii*) It has been observed that the value of $k_{s,h}$ records a decrease with the increasing concentration of the supporting electrolytes, viz., NaCl, $NaNO_3$, KNO_3, KBr, KH_2PO_4, pot. acetate, pot. benzoate. The values of $k_{s,h}$ (cm/sec) for these electrolytes, in the concentration range 0.05-1.0 *M*, lie between $10.90 \times 10^{-3} - 5.72 \times 10^{-3}$; $4.65 \times 10^{-3} - 4.0 \times 10^{-3}$; $6.36 \times 10^{-3} - 5.32 \times 10^{-3}$; $6.78 \times 10^{-3} - 5.32 \times 10^{-3}$; $5.66 \times 10^{-3} - 5.12 \times 10^{-3}$; $6.67 \times 10^{-3} - 4.12 \times 10^{-3}$ and $5.63 \times 10^{-3} - 4.93 \times 10^{-3}$ respectively, while the values of 'α' lie between 0.4384 – 0.4246 ; 0.3500 – 0.3408 ; 0.4525 – 0.4396 ; 0.4036 – 0.3776 ; 0.4386 – 0.4270 ; 0.4745 – 0.4136 and 0.4612 – 0.4412. From this it follows that the rate of the electrode reaction is retarted at increased concentrations of these supporting electrolytes. This suggests that with the increase in the concentration of the supporting electrolyte, the quasi-reversible electrode reaction is gradually pushed towards irreversibility. The decrease in the value of 'α' with increasing concen-

trations of the supporting electrolytes lends fnrther support to this conclusion[11].

However, the value of $k_{s,h}$ increases with increasing concentration of the following supporting electrolytes :

$NaClO_4$, $KClO_4$ KNO_3, KI, NH_4CNS, NH_4Cl, NH_4NO_3, pot. tartrate, pot. citrate, $Mg(NO_3)_2$, $Ca(NO_3)_2$, $Sr(NO_3)_2$ and $Ba(NO_3)_2$.

The values of $k_{s,h}$ (cm/sec) for these electrolytes, in the concentration range 0.05 – 1.0*M*, lie between $7.94 \times 10^{-3} - 9.62 \times 10^{-3}$; $6.18 \times 10^{-3} - 6.85 \times 10^{-3}$; $4.32 \times 10^{-3} - 6.21 \times 10^{-3}$; $5.72 \times 10^{-3} - 6.43 \times 10^{-3}$; $5.65 \times 10^{-3} - 6.28 \times 10^{-3}$; $4.67 \times 10^{-3} - 7.68 \times 10^{-3}$; $5.42 \times 10^{-3} - 5.96 \times 10^{-3}$; $4.81 \times 10^{-3} - 5.86 \times 10^{-3}$; 4.18×10^{-3} 5.40×10^{-3} ; $5.10 \times 10^{-3} - 5.42 \times 10^{-3}$; $5.12 \times 10^{-3} - 5.34 \times 10^{-3}$; $5.88 \times 10^{-3} - 6.42 \times 10^{-3}$ and $5.00 \times 10^{-3} - 6.25 \times 10^{-3}$ respectively, while the values of 'α' lie between 0.4240 – 4490 ; 0.4210 – 0.4426 ; 0.4356 – 0.4835 ; 0.4360 – 0.4475 ; 0.3460 – 0.3680 ; 0.3950 – 0.4384 ; 0.3865 – 0.4256 ; 0.4165 – 0.4438 ; 0.4545 – 0.4786 ; 0.3512 – 0.3685 ; 0.3200 – 0.3570 ; 0.3350 – 0.3730 and 0.3758 – 0.4215. An increase in the value of $k_{s,h}$ implies that the electrode reaction of Mn(II) tends towards reversibility at increased concentrations of the above supporting electrolytes. The increase in the value of 'α' with increasing concentration of these supporting electrolytes is in conformity with this conclusion.

Taking different sets of supporting electrolytes such that when cation was varied anion remained identical and vice-versa, the effect of anions and cations at a certain concentration (0.1*M*) on the value of $k_{s,h}$ has been attempted.

The order of $k_{s,h}$ value is as follows :

(i) For univalent cations : $NH_4^+ > K^+ > Na^+$ (in nitrates)

(ii) for bivalent cations : $Sr^{2+} > Ba^{2+} > Ca^{2+}$; Mg^{2+}

(iii) for anions (in pot. salts) : $ClO_4^- > I^-$; $NO_2^- > CH_3COO^- > NO_3^- >$ tart.$^{2-} > C_6H_5COO^-$; $H_2PO_4^- >$ citr.$^{3-} > Cl^- > Br^-$.

Acknowledgement

Thanks are due to the Principal, Agra Colleg Agra, for providing necessary facilities and also t U. G. C. for the award of a contingency grant t one of them (M. S.).

References

1. J. N. GAUR and D. S. JAIN, *Indian J. Appl. Chem.*, 196 **28**, 123.
2. J. N. GAUR and N. K. GOSWAMI, *J. Indian Chem. Soc* 1969, **46**, 1030.
3. J. N. GAUR, P. S. VERMA and D. S. JAIN, *Indian Chem.*, 1975, **13**, 586.
4. J. KORYTA, *Electrochim. Acta*, 1962, **6**, 67.
5. J. E. B. RANDLES and K. W. SOMERTON, *Trans. Fara Soc*, 1952, **48**, 951.
6. S. S. SHARMA and M. SINGH, *J Indian Chem. Soc.*, 197 **53**, 693.
7. L. MEITES, 'Polarographic Techniques', Interscience Publ New York, 1965, p. 217.
8. R GOTO and I. TACHI, Proc. Intern. Polarogr. Cong Vol. 1, 1951, p. 69.
9. P. J. GELLINGS, Z. Elektrochim. Ber. Bunsenges. *Phys Chem.*, 1962, **66**, 477, 481, 799 and 1963, **67**, 167.
10. P. DELAHAY, *J. Amer. Chem. Soc.*, 1953, **75**, 1430.
11. S. K. JHA and S. N. SRIVASTAVA, *Z. Naturforsch.*, 1975 **30b**, 859.

J. Indian Chem. Soc.,
Vol. LVII, January 1980, pp. 23-25

Glycolate Complexes of La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III) and Lu(III)

C. PANDA AND R. K. PATNAIK

Department of Chemistry, Regional Engineering College, Rourkela-769 008

Manuscript received 21 August 1979, accepted 30 November 1979

The formation of 1 : 1 and 1 : 2 complexes of rare earth ions ($M^{3+} = La^{3+}$, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+} and Lu^{3+}) with glycolic acid (HG) have been studied *p*H metrically. The equilibrium constants for the reactions

$$M^{3+}+HG \overset{k}{\rightleftharpoons} MG^{2+}+H^+, \quad MG^{2+} \overset{k_1}{\rightleftharpoons} MG^+ + H^+ \text{ and}$$
$$M^{3+}+2HG \rightleftharpoons MG_2^+ + 2H^+ \text{ and } MG_2^+ \rightleftharpoons MG_2 + H^+$$

have been determined.

MOELLER[1] has reviewed the rare earth complexes. Some attempts have been made on the structural study[2-3] and on the determination of thermodynamic functions[4] of the rare earth glycolates. The present communication reports the formation constants of 1 : 1 and 1 : 2 rare earth glycolate complexes by *p*H measurement method.

Experimental

The rare earth nitrates (99.99% pure) were obtained from the Indian Rare Earth Ltd. and Research Organic/Inorganic Chemical Corporation, U.S.A. *p*H titrations were performed at $32 \pm 1°$ with a digital *p*H meter (ECI-Model 822A) in nitrogen atmosphere after maintaining an ionic strength of 0.1*M* by the addition of potassium nitrate.

Results and Discussion

Determination of formation constants of 1 : 1 complexes :

The reaction taking place due to the interaction of the rare earth ions with glycolic acid can be represented as :

$$M^{3+}+HG \rightleftharpoons C+nH^+ \qquad \dots (1)$$

where C is the complex formed and n is the number of protons liberated per gm atom of the rare earth metal ions. The values of n are calculated by the method followed in the cadmium citrate complex[5] and gluconate complexes of yttrium[6], praseodymium, and neodymium[7], samarium, gadolinium, dispro-sium and holmium[8] using the equation

$$\frac{\Delta[NaOH] - a/b\,\Delta[TG]}{[C]} = n - a/b \qquad \dots (2)$$

where $a = \frac{k}{[H^+]}$ and $b = 1 + \frac{k}{[H^+]}$ and *p*k for glycolic acid[9] is 3.71. Δ[NaOH], and Δ[TG] are the difference in the molar concentrations of sodium hydroxide and total glycolate at two points on the same axis of curves B and A. [C] and [M] represent the molar concentrations of the complex and metal salt respectively.

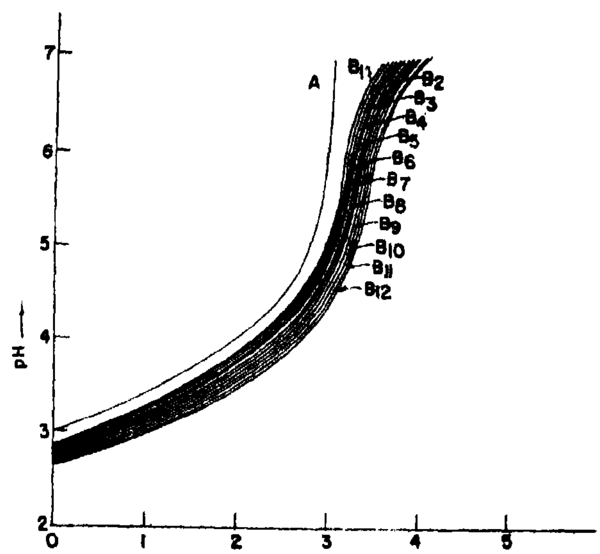


Fig.1 0.1M NaOH added ml.

Fig. 1. *p*H titration of 50.00 ml of solution containing 5.0×10^{-3} g mole of potassium nitrate and 3.125×10^{-4} g. mole of glycolic acid (Curve A) and that of same volume of twelve other solutions each containing the same quantities of the above constituents and 2.5×10^{-4} g. mole of rare earth nitrate against 0.1 *M* sodium hydroxide. B_1 – La(III), B_2 – Ce(III), B_3 – Pr(III), B_4 – Nd(III), B_5 – Sm(III), B_6 – Gd(III), B_7 – Dy(III), B_8 – Ho(III), B_9 – Er(III), B_{10} – Tm(III), B_{11} – Yb(III) and B_{12} – Lu(III).

When the formation of the complex is complete

$[C] = [\text{Metal salt}]$

Hence, $\frac{\Delta[NaOH] - a/b\Delta[TG]}{[\text{Metal salt}]} = n - a/b$

The values of n are more than one beyond *p*H 4.6, 4.6, 4.4, 4.4, 4.4, 4.6, 4.2, 4.2, 4.2, 3.8, 3.8 and 3.6 respectively for La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III) and Lu(III) respectively. Below these *p*H values the reaction (1) may be represented as

$$M^{3+} + HG \rightleftharpoons C^{2+} + H^+ \quad \dots (3)$$

and $$K = \frac{[C^{2+}][H^+]}{[M^{3+}][HG]} \quad \dots (4)$$

Assuming n to be one below these *p*H values, $[C^{2+}]$ is calculated. $[M^{3+}]$ is obtained by subtracting $[C^{2+}]$ from $[M(NO_3)_3]$.

The negative logarithm values of the equilibrium constants, K, were calculated by the equation (4) and the values with the standard deviation are 1.58 ±0.03, 1.37±0.06, 1.17±0.10, 0.94±0.05, 0.87±0.07, 1.19±0.05, 0.75±0.12, 0.67±0.14, 0.63±0.06, 0.38±0.10, 0.32±0.11 and 0.17±0.04, respectively for La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III) and Lu(III) systems.

In the *p*H ranges, 4.8-6.8, 4.8-6.4, 4.6-6.65, 4.6-6.9, 4.4-6.8, 4.6-7.0, 4.4-6.45, 4.4-6.3, 4.4-6.0, 4.0-6.56, 4.0-6.33 and 3.8-6.05 for the above systems La(III)-Lu(III) respectively, n is >1 but <2. Hence in the *p*H ranges, the complex, C^{2+}, dissociates to C^+ and a proton

$$C^{2+} \rightleftharpoons C^+ + H^+ \quad \dots (5)$$

It can be shown as before that

$$K_1 = \frac{[C^+][H^+]}{[C^{2+}]} = \frac{(n-1)[H^+]}{(2-n)} \quad \dots (6)$$

The $-\log K_1$ values calculated by the equation (6) are found to be 6.64±0.17, 6.38±0.08, 6.36±0.22, 6.25±0.16, 6.01±0.15, 6.34±0.06, 5.89±0.12, 5.76±0.12, 5.70±0.09, 5.55±0.09, 5.40±0.04 and 5.14±0.10 for La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III) and Lu(III) systems respectively. The hydroxide of the metals are precipitated at *p*H, 6.60, 6.40, 6.65, 6.90, 6.80, 7.00, 6.45, 6.30, 6.0, 6.56, 6.33 and 6.05 respectively for La(III)-Lu(III) systems.

Determination of formation constants of the 1 : 2 rare earth glycolate complexes :

The reaction taking place in the formation of 1 : 2 glycolate complexes can be represented as

$$M^{3+} + 2HG \rightleftharpoons C_{(1:2)} + nH^+ \quad \dots (7)$$

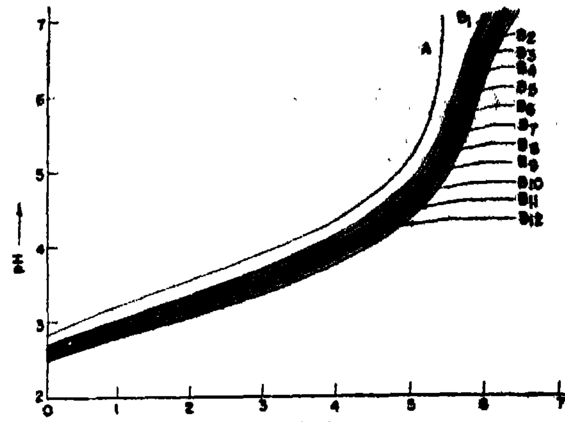


Fig. 2. *p*H titration of 50.00 ml of solution containing 5.0×10^{-3} g. mole of potassium nitrate and 5.65×10^{-4} g. mole of glycolic acid (Curve-A) and that of same volume of twelve other solutions each containing the same quantities of the above constituents and 2.5×10^{-4} g. mole of rare earth nitrate against 0.1 *M* sodium hydroxide. B_1 – La(III), B_2 – Ce(III), B_3 – Pr(III), B_4 – Nd(III), B_5 – Sm(III), B_6 – Gd(III), B_7 – Dy(III), B_8 – Ho(III), B_9 – Er(III), B_{10} – Tm(III), B_{11} – Yb(III) and B_{12} – Lu(III).

The values of n were calculated by the equation (8).

$$\frac{\Delta[NaOH] - a/b\Delta[TG]}{[M(NO_3)_3]} = n - 2a/b \quad \dots (8)$$

Above *p*H 4.6, 4.6, 4.4, 4.4, 4.6, 4.6, 4.6, 4.4, 4.2, 4.0, 4.0 and 3.8 for the above systems La(III)-Lu(III), respectively the value of n is greater than 2. Below these *p*H values the reaction (7) may be represented as

$$M^{3+} + 2HG \rightleftharpoons C^+_{1:2} + 2H^+ \quad \dots (9)$$

and

$$K^* = \frac{[C^+_{1:2}][H^+]^2}{[M^{3+}][HG]^2}$$

Assuming the value of n to be 2 below these *p*H values, the $-\log K^*$ values were calculated and are found to be 2.56±0.06, 2.29±0.07, 2.14±0.09, 2.09 ±0.09, 2.05±0.06, 2.43±0.09, 2.22±0.10, 2.10±0.05, 1.90±0.05, 1.64±0.05, 1.59±0.05, and 1.33±0.03 for La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III) and Lu(III) systems respectively.

In the *p*H ranges, 4.8-6.6, 4.8-6.', 4.6 -6.65, 4.6-6.9, 4.8-6.8, 4.8-7.0, 4.8-6.45, 4.6-6.3, 4.4-6.0, 4.2-6.56 4.2-6.33 and 4.0-6.05 systems respectively the n values are >2 but <3. So in these *p*H ranges the complex, $C^+_{1:2}$ dissociates to $C_{1:2}$ and H^+ according to the reaction (10).

$$C^+_{1:2} \rightleftharpoons C_{1:2} + H^+ \quad \dots (10)$$

and

$$K_1^* = \frac{[C_{1:2}][H^+]}{[C^+_{1:2}]}$$

The $-\log K_1$ values calculated as before are found to be 6.26 ± 0.10, 5.95 ± 0.04, 5.80 ± 0.07, 5.78 ± 0.08, 5.74 ± 0.04, 6.08 ± 0.07, 5.71 ± 0.05, 5.70 ± 0.06, 5.61 ± 0.16, 5.48 ± 0.12, $5.36\pm0.0/$ and 5.23 ± 0.10 for La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III) and Lu(III) systems respectively. The relative order of stabilities is as expected.

Acknowledgement

The auhors are thankful to the Government of India and U. G. C., New Delhi for financial assistance.

References

1. T. Moeller, D. F. Martin, L. C. Thompson, R. Ferrus, G. R. Feistel and W. J. Randall, *Chem. Rev.*, 1965, **65**(1), 1.
2. G. Ingmar, *Acta. Chem. Scand*, 1972, **26**(4), 1479 ; *Chem. Abs.*, 1972, **77**, 415.
3. K. I. Petrov, M. G. Zaitseva, T. V. Shestakova and Z. N. Prozorovskaya, *Zh. Neorg. Khim.*, 1973, **18**(10), 2753 ; *Chem. Abs.*, 1974, **80**, 307.
4. R. Mukner, *J. Inorg. Nuclear Chem.*, 1972, **34**(3), 973.
5. R. K. Patnaik and S. Pani, *J. Indian Chem. Soc.*, 1957, **34**, 673.
6. G. Panda and R. K. Patnaik, *J. Indian Chem. Soc.*, 1977, **54**(9), 843.
7. C. Panda and R. K. Patnaik, *J. Indian Chem. Soc.*, 1976, **53**(11) 1079.
8. C. Panda and R. K. Patnaik, *J. Indian Chem. Soc.*, 1979, **56**(2), 183.
9. R. K. Cannan and A. Kibrick, *J. Amer. Chem. Soc.*, 1938, **60**, 2314.

J. Indian Chem. Soc.,
Vol. LVII, January 1980, pp. 26-28

Dioxouranium(VI) and Thorium(IV) Complexes with a Tri-dentate Ligand

HRUDANANDA MOHANTA* AND KAILASH C. DASH†

Department of Chemistry, Bhadrak College, Bhadrak-756 100, India

Manuscript received 17 August 1979, accepted 30 November 1979

New dioxouranium(VI) and thorium(IV) complexes with a dibasic tri-dentate ligand, H_2L, *derived by the condensation of anthranilic acid and salicylaldehyde were prepared* and characterised. The ligand behaved as a neutral one when reacted with UO_2X_2 forming 10-coordinated complexes of the type $UO_2(H_2L)_2X_2$ (X = *Cl*, I, NCS, NO_3, ClO_4, 0.5 SO_4) and with UO_2Ac_2 it formed 8-coordinated $UO_2(HL)_2$, acting as a deprotonated, uninegative, *tridentate* ligand. The latter form of coordination also takes place on reaction with ThX_4 *to form complexes of the type* $Th(HL)_2X_2$, n H_2O (X = Cl, I, NCS, NO_3, ClO_4 and n = 2, 3 or 4). These water molecules are only loosely held by the metal ion and all of them are lost on heating at 120°. The Th(IV) complexes are thus all 8-coordinated.

COMPOUNDS of amino acids with transition metal ions are well known[1], but those of the Schiff bases of amino acids are not as common[2]. Further, not many Schiff base complexes of the 4f- or 5f-inner transition elements are known[3,4]. Very rarely, the Schiff bases coordinate as the neutral molecules, the usual form being the deprotonated anions of the Schiff base. As a part of our study of dioxo-uranium(VI) and thorium(IV) complexes with multi-dentate ligands having 2 to 6 donor sites, we have already reported[5-7] complexes with several Schiff bases and now report the synthesis and characterisation of a series of complexes with a potential tri-dentate ligand, anthranilic acid salicylidene imine H_2L (donor set NO_2) derived by the condensation of salicylaldehyde and anthranilic acid. The ligand coordinates either as a neutral molecule to form complexes $UO_2(H_2L)X_2$ (X = Cl, I, NCS, NO_3, ClO_4, 0.5SO_4) or as a uninegative ion (HL^-) to form complexes of the type $UO_2(HL)_2$ or $Th(HL)_2X_2.nH_2O$ (X = Cl, I, NCS, NO_3, ClO_4). The compounds have been characterised by analytical data, electrical conductivity and IR spectral measurements, and the stoichiometry as well as the coordination number assigned.

Experimental

Hydrated thorium(IV) and uranyl(VI) chloride, nitrate and uranyl sulphate were B.D.H. reagent grade. The iodide, thiocyanate, perchlorate of uranyl(VI) and thorium(IV) were prepared as described earlier[5-7].

The ligand anthranilic acid salicylaldehyde (H_2L) was prepared by adding an alcoholic solution of salicylaldehyde dropwise to an ethanolic solution of anthranilic acid. The resulting orange solution was refluxed for 6 hours and on slow evaporation the desired orange-red crystalline compound separated out, which was filtered washed several times with alcohol and dried *in vacuo.*

The C, H, N analyses were carried out at Würzburg University, W. Germany. The metal (uranium and thorium) and the anion (Cl^-, Br^-, I^-, NO_3^-, ClO_4^-, $SO_4^=$) were estimated as described[5-7]. The electrical conductivity, IR spectra and electronic spectra were measured as usual[5].

Preparation of the complexes :

The complexes were prepared by mixing, warm ethanolic solution of the appropriate metal salt with the ligand in ethanol medium (1 : 2.5 ratio). In almost all cases the complexes appeared on stirring and in few cases refluxing was required. The complexes were filtered, washed with alcohol followed by ether and dried in *vacuo*. The anhydrous thorium(IV) complexes were prepared by keeping the hydrated complexes in an air-oven at 120° for several hours to constant weight.

Results and Discussion

The complexes isolated are presented in Tables 1 and 2 alongwith their characterising data. All the compounds have an intense yellow or orange-yellow colour, they are high melting (>260°) and quite stable. The electrical conductance values in CH_3NO_2 or DMF solutions adequately confirmed the non-electrolytic nature of the complexes[8]. The electronic spectra in methanol were found to be similar to each other in regard to band shapes and positions. The Th(IV) complexes contain either 2,3 or 4 molecules of water of crystallisation and all

† Present address : Anorg. Chem. Inst. Technischen Universitat Munchen, Lichtenbergstr-4, D-8046, Garching, W. Germany.

TABLE 1—CHARACTERISING DATA FOR DIOXOURANIUM(VI) COMPLEXES

Compound	Analyses(%) Found (calc.)					Λ_m in $MeNO_2$ (Ω^{-1} mole^{-1} cm^2)
	U	C	H	N	X	
$UO_2(H_2L)_2Cl_2$	29.2 (28.9)	40.4 (40.8)	2.8 (2.6)	3.7 (3.4)	8.4 (8.6)	11.5
$UO_2(H_2L)_2I_2$	23.8 (23.6)	33.1 (33.4)	2.2 (2.1)	2.5 (2.7)	25.0 (25.3)	15.0
$UO_2(H_2L)_2(NCS)_2$	27.4 (27.4)	41.7 (41.4)	2.4 (2.5)	6.0 (6.4)	13.8 (13.8)	20.6
$UO_2(H_2L)_2(NO_3)_2$	27.5 (27.1)	38.0 (38.3)	2.5 (2.5)	6.5 (6.3)	14.0 (14.1)	21.2
$UO_2(H_2L)_2SO_4$	28.4 (28.0)	39.2 (39.6)	2.4 (2.5)	3.4 (3.3)	11.5 (11.3)	44*
$UO_2(H_2L)_2(ClO_4)_2$	27.5 (28.0)	39.1 (39.4)	2.6 (2.5)	3.0 (3.2)	23.1 (23.3)	10.7
$UO_2(HL)_2$	32.0 (31.7)	44.5 (44.7)	2.8 (2.6)	3.5 (3.7)	—	3.4*

* Conductance values in DMF.

ν(C≡N) and ν(C–S) vibrations of a *N*-coordinated terminally bonded isothiocyanate[10]. The nitrato complexes exhibit bands at 1460, 1280, 1045, 820 and 730 cm^{-1} showing evidences for unidentate coordination (C_{2v}) of the nitro group[12]. The bidentate coordination of the sulphato group[13,14] (C_{2v}) in $UO_2(H_2L)SO_4$ is evident from the appearance of the bands at 1175, 1155, 1075 and 650 and 610 cm^{-1} regions. The $UO_2(H_2L)_2(ClO_4)_2$ and the $Th(HL)_2(ClO_4)_2$ complexes contain the ClO_4^- group which are coordinated in a unidentate manner[14] as is clear from their IR spectra observed at 1135, 1110, 1020 and 620 cm^{-1} region.

Thus, a series of uranyl complexes having a coordination number of 8 or 10 and a series of thorium(IV) complexes having a coordination number of 8, are isolated where the ligand is coordinated in a tri-dentate manner either as neutral molecule or as a deprotonated, uninegative anion.

TABLE 2—CHARACTERISING DATA FOR THORIUM(IV) COMPLEXES

Compound	Analyses(%), Found (calc.)					%loss of H_2O at 120°C	Λ_m in $MeNO_2$ (Ω^{-1} mol^{-1} cm^2)
	Th	C	H	N	X		
$Th(HL)_2Cl_2.4H_2O$	26.6 (26.2)	39.0 (39.2)	3.1 (3.2)	3.3 (3.2)	8.3 (8.0)	8.1 (8.1)	10
$Th(HL)_2I_2.2H_2O$	22.5 (22.7)	33.1 (33.5)	2.2 (2.3)	2.5 (2.7)	25.0 (25.3)	3.5 (3.5)	14
$Th(HL)_2(NCS)_2.2H_2O$	27.0 (26.9)	42.1 (42.5)	3.0 (2.8)	6.3 (6.6)	13.4 (13.7)	4.2 (4.2)	51
$Th(HL)_2(NO_3)_2.3H_2O$	26.4 (26.0)	37.9 (37.6)	3.0 (2.8)	6.1 (6.2)	13.4 (13.9)	5.9 (6.0)	9
$Th(HL)_2(ClO_4)_2.2H_2O$	24.1 (24.5)	35.7 (35.4)	2.8 (2.5)	3.1 (3.0)	21.5 (21.1)	3.7 (3.8)	9

of them are lost quantitatively by heating the hydrated complexes at 120°. They are not bound to the metal ion as is clear from the IR spectra of the hydrated complexes.

The IR spectra of the ligand and the complexes were investigated. In all cases ν(OH) was obtained as a weak band in 3300-3400 cm^{-1} region, ν(C=N) in the 1610-1625 cm^{-1} region, ν(C–O) in the 1180 cm^{-1} region, $\nu_{as}(COO^-)$ in 1590 cm^{-1} region and $\nu_s(COO^-)$ in the 1380-1410 cm^{-1} region. In addition, ν(C–N) at 1270 cm^{-1}, ν(C–H) at around 3000 cm^{-1} and the phenyl ring vibrations at 1500 cm^{-1} region were observed. These indicate the tri-dentate coordination of the ligand in the complexes. The uranyl vibrations were observed at about 920 cm^{-1} and 810 cm^{-1} corresponding to ν_{as}(U–O) and ν_s(U–O) vibrations, respectively[9] in good agreement with the linear nature of the UO_2^{++} group.

The thiocyanate complexes exhibit bands at 2040 and 835 cm^{-1} for the dioxouranium(VI) complex and at 2050, 2030 and 840 cm^{-1} for the thorium(IV) complex corresponding to the

Acknowledgement

Our thanks are due to F. E. Ullrich, Anorg. Chem. Institut, Würzburg (W. Germany) for carrying out the C, H, N analyses of all the compounds.

References

1. K. NAKAMOTO, Y. NORIMOTO and A. E. MARTELL, *J. Amer. Chem. Soc.*, 1961, **83**, 4528.
2. R. H. HOLM, G. W. EVERETT, JR. and A. CHAKRAVORTY *Prog. Inorg. Chem.*, (Ed. F. A. COTTON, Wiley, New York, 1966, Vol. 7, p. 83).
3. A. E. COMYNS, *Chem. Rev.*, 1960, **60**, 115.
4. A. K. MUKHERJEA and P. RAY, *J. Indian Chem Soc.*, 1977, **54**, 166.
5. H. N. MOHANTA and K. C. DASH, *Indian J. Chem.*, 1977, **15A**, 657 ; *J. Indian Chem. Soc.*, 1977, **54**, 166.
6. H. N. MOHANTA and K. C. DASH, *J. Inorg. Nuclear Chem.*, 1977, **39**, 1345 ; *Synth. React. Inorg. Metal-Org. Chem.*, 1978, **8**, 43.

7. K. C. DASH and H. N. MOHANTA, *Trans. Met. Chem.*, 1977, 2, 229.
8. W. J. GEARY, *Coord. Chem. Revs.*, 1971, 7, 81.
9. J. L. BULLOCK and F. W. PARRETT, *Canad. J. Chem.*, 1970, 48, 3095.
10. R. A. BAILEY, S. L. KOZAK, T. W. MICHELSEN and W. N. MILLS, *Coord. Chem. Revs.*, 1971, 6, 407.
11. M. CHOCA and J. R. FERRARO, *J. Chem. Soc.*, (Dalton), 1972, 2297.
12. G. C. BARRACLOUGH and M. L. TOBE, *J. Chem. Soc.*, 1961, 1993.
13. E. P. HERTZENBERG and J. C. BAILAR, JR., *Inorg. Chem.*, 1971, 10, 2371.
14. B. J. HATHAWAY and A. E. UNDERHILL, *J. Chem. Soc.*, 1961, 3091.

J. Indian Chem. Soc.,
Vol. LVII, January 1980, pp. 29-31

Preparation and Characterisation of Some Mixed Ligand Complexes of Transition Metals. Part (III) : Complexes of Copper(II) Succinate with Aniline, Toluidines and Pyridine

(MRS.) P. R. SHUKLA AND A. M. JAISWAL

Chemistry Department, Lucknow University, Lucknow, India

Manuscript received 17 August 1979, accepted 30 November 1979

Five complexes of Copper(II) succinate of the type CuSucc. $(am)_2$ where 'am' stands for any of the above mentioned amines have been prepared in methanol solutions and crystallised. The complexes have been characterised and assigned above formula on the basis of elemental analysis and molar conductance data. The co-ordination of succinate ion and amines to Copper(II) is indicated by the infrared spectra while magnetic and spectroscopic measurements indicates nearly planer geometries for the complexes.

IN the past one decade the interest of transition metal complexes is shifting from the use of inorganic anions to organic anions and a large number of complexes of organic anions such as phthalimide, succinimide, oxalate, formate, benzoate and phthalate with first transition series metals have been reported from this laboratory[1-11]. We have now undertaken the study of transition metal succinates and their complexes. The succinate ion, like phthalate ion, contains two COO^- groups and is thus expected to have as a bidentate ligand itself, occupying any two adjacent positions in the coordination geometry of Copper(II). The amines are thus left with other two available positions. The present paper records the preparation of five complexes of Copper(II) succinate with amines as aniline ; *o*-, *m*-, *p*-toluidines and pyridine, which have been fully characterised by using conductivity, infrared, magnetic and electronic spectral data.

Experimental

Copper(II) succinate was prepared by adding an aqueous solution of Sodium(I) succinate to Copper(II) sulphate. The blue compound was filtered, washed repeatedly with water, dried and analysed and its formula worked out to be Cu Succinate. $2H_2O$.

This was suspended in methanol, a little more than the calculated quantity of amine was added and the solution refluxed for few hours. The complex was crystallised out from this solution, analysed and the results of analysis are given below :

1. *Succinate bi(aniline) Copper(II)* : Cu = 17.82% ; C = 50.90% ; H = 5.02% ; N = 7.23% ; $CuC_{16}H_{18}N_2O_4$ requires Cu = 17.38% ; C = 51.95% ; H = 4.92% and N = 7.66%.

Colour – Green

2. *Succinate bi(o-toluidine) Copper(II)* : Cu = 16.40% ; C = 54.80% ; H = 6.02% ; N = 8.10% ; $CuC_{18}H_{22}N_2O_4$ requires Cu = 16.14% ; C = 54.91% ; H = 5.59% and N = 7.11%.

Colour – Greenish blue

3. *Succinate bi(m-toluidine) Copper(II)* : Cu = 16.82% ; C = 54.28% ; H = 5.72% ; N = 7.65% ; Cu $C_{18}H_{22}N_2O_4$ requires Cu = 16.14% ; C = 54.91% ; H = 5.59% ; N = 7.11%.

Colour – Greenish blue

4. *Succinate bi(p-toluidine) Copper(II)* : Cu = 16.82% ; C = 54.08% ; H = 5.98% ; N = 6.89% ; Cu $C_{18}H_{22}N_2O_4$ requires Cu = 16.14% ; C = 54.91% ; H = 5.59% ; N = 7.11%.

Colour – Olive green

5. *Succinate bi(pyridine) Copper(II)* : Cu = 18.50% ; C = 49.28% ; H = 4.94% ; N = 8.69% ; $CuC_{14}H_{14}N_2O_4$ requires Cu = 18.82% ; C = 49.78% ; H = 4.14% and N = 8.29%.

Colour – Light blue

Conductivities were measured in nitrobenzene at a concentration of $10^{-3}M$ on a Philips PR 9500 magic eye type instrument and values given in Table 1.

TABLE 1—MAGNETIC AND ELECTRONIC SPECTRAL DATA

Complexes	Molar conductance in mhos	μ_{eff} in B.M.	λ_{max}	Frequency in cm^{-1}	Dq in cm^{-1}
$CuC_4H_4O_4(aniline)_2$	1.5	1.845	696	14,370	1437
$CuC_4H_4O_4(o\text{-tolu.})_2$	2.0	1.855	705	14,170	1417
$CuC_4H_4O_4(m\text{-tolu.})_2$	0.9	1.871	715	13,582	1358
$CuC_4H_4O_4(p\text{-tolu.})_2$	0.8	1.886	698	14,320	1432
$CuC_4H_4O_4(Py)_2$	1.0	1.921	660	15,310	1531

I. R. and electronic spectra were recorded on a Perkin-Elmer model 221 in a region 4000-400 cm^{-1} and on VSU 12 spectrometer in the form of solid sample respectively. The magnetic measurements were made on powdered samples by using Gouy's method and these values are given in Table 1.

Results and Discussion

The percentage of constituents elements show the molecular formula to be Cu Succ(am)$_2$ while the molar conductance values are in the usual range of nonelectrolytic complexes. It thus appears that the succinate ion is also co-ordinated along with the amines and the formulae are [Cu. Succ.(am)$_2$]. Further evidences for the co-ordination of ligands is obtained from the infrared spectra as discussed below.

I. R. spectra of succinate ion :

The succinate ion belongs to high symmetry point group $C_2\lambda$ and due to the presence of a center of symmetry passing through the ion, these absorption bands which are symmetric across the center are forbidden in the I. R. spectra. The CH_2 bending and COO^- symmetric stretchings which are observed in the form of strong peak at 1438 cm^{-1} and a shoulder on its longer wave length side in Sodium(I) succinate are shifted to lower wave lengths in co-ordination. Two or even three bands are observed in the complexes with medium to strong intensity in the range 1420-1360 cm^{-1} thus undergiving a negative shift of about 60 cm^{-1}. This is due to the co-ordination of the ion[12,13]. The sharp bands at 1226 cm^{-1} and 1176 cm^{-1} of sodium succinate are assigned to CH_2 Wagging and twisting frequencies respectively. In complexes both these are split and shifted to higher frequencies by about 100 cm^{-1}, and appears at 1300 & 1275 cm^{-1} which confirms the co-ordination, as bands in the above range are characteristic of co-ordinated carboxylate ion[14]. In addition to these each complex also shows a medium to strong band at 805 cm^{-1} attributable to CH_2 rocking, which is due to the trans configuration of the carbon chains.

I. R. of aniline and toluidine complexes :

A very sharp band is seen in all the complexes around 3310 cm^{-1} due to NH stretch. The negative shift of the band by 150 cm^{-1} is an indication of co-ordination[16]. The NH deformation vibrations are seen in the region 1600-1580 cm^{-1} in the free ligand. Co-ordination is known to cause a positive shift in these and hence in complexes, one sharp band is seen at 1605 cm^{-1} due to this mode. The NH bending models are also found to be shifted to higher frequency due to co-ordination and out of the three such vibrations the NH rocking is seen around 750 cm^{-1}. It is thus clear that the positions of all these bands suggest co-ordination of the ligand [16,17].

I. R. spectra of pyridine complexes :

The co-ordination of pyridine molecule to metals is known to cause a tightening of the aromatic ring and hence the important bands undergo positive shift[18] some such bands which indicate co-ordination are as follows :

(a) Between 1430-1640 cm^{-1}, four bands are seen in free pyridine which are due to C=C, C=N and ring stretchings. The 1625 cm^{-1} and 1593 cm^{-1} bands of pyridine, which are combination bands (60+12 or 1+6b) merge together and appear as a single band at 1635 cm^{-1}. The weak band at 1570 cm^{-1} of pyridine does not appear in the complex but the 1578 cm^{-1} band undergoes positive shift and occurs at 1600 cm^{-1}.

(b) The ring breathing models at 995 cm^{-1} shifts to 1010 cm^{-1} in complex, while the three C–H deformations at 1217 cm^{-1}, 1145 cm^{-1} and 1068 cm^{-1} in free ligand appear in complex with positive shift at 1295, 1158 and 1070 cm^{-1}[19].

From the above discussion it follows that complexes are tetra co-ordinated, two co-ordination positions are occupied by succinate ion and other two by amines. The complexes are all paramagnetic μ_{eff} lying in the range 1.845-1.921 B.M. suggesting a planer geometry for complexes.

The diffuse reflactance spectra contain only one main but very broad band in the region 12.50-20 kK, the position of which depends upon the crystal field strength of amines, on theoretical considerations three bands are expected corresponding to the transitions ; in the planer geometry-

$$^2B_{1g} \rightarrow {}^2B_{2g}$$
$$^2B_{1g} \rightarrow {}^2E_g$$
$$^2B_{1g} \rightarrow {}^2A_{1g}$$

which in the present complexes are grouped together in one absorption envelope and appear in the form of a single very broad band [20,21]. The position of this band however rules out the tetrahedral structures as the same are expected to give one band in the near I.R. region at 9.00 kK[22].

The position of this absorption band is equal to Dq, which thus comes out to be around 1250 cm^{-1}. It is, however, found that the Dq values obtained for the aniline and toluidine complexes are lower than the corresponding values for pyridine complexes, which is in agreement with positions of these amines in spectrochemical series.

Acknowledgement

One of us (AMJ) is thankful to Principal and Head, Chemistry Department, B.S.N.V. Degree College, Lucknow for providing facilities for some of the experiments.

References

1. P. R. SHUKLA, M. P. KHARE and L. N. SRIVASTAVA, *J. Prakt. Chem.*, 1965, **28**, 21.

2. P. R. SHUKLA, M. P. KHARE and L. N. SRIVASTAVA, *J. Prakt. Chem.*, 1965, **29**, 83.

3. P. R. SHUKLA, M. P. KHARE and L. N. SRIVASTAVA, *Z. Physik. Chem*, 1967, **234**, 153.

4. P. R. SHUKLA, M. P. KHARE and L. N. SRIVASTAVA, *Z. Physik. Chem.*, 1967, **237**, 158.

5. P. R. SHUKLA and L. N. SRIVASTAVA, *Z. anorg. allg. Chem.*, 1964, **333**, 161.

6. P. R. SHUKLA, GOPAL NARAIN and L. N. SRIVASTAVA, *J. Prakt. Chem.*, 1966, **31**, 123.

7. P. R. SHUKLA and GOPAL NARAIN, *J. Indian Chem. Soc.*, 1967, **44**, 652.

8. P. R. SHUKLA and GOPAL NARAIN, *Aust. J. Chem.*, 1967, **20**, 227.

9. P. R. SHUKLA and GOPAL NARAIN, *Indian J. Chem.*, 1967, **5**, 593.

10. P. R. SHUKLA and RAJ KAMAL, *J. Indian Chem. Soc.*, 1978, **55**, 871(1).

11. P. R. SHUKLA and RAJ KAMAL, under Publication, *J. Indian Chem. Soc.*, (1979).

12. J. K. BROWN and N. SHEPPARD, *Trans. Faraday Soc.*, 1952, **48**, 128.

13. Y. KUSODA and M. KUBO, *J. Polymer Sc.*, 1967, **26**, 82.

14. S. F. A. KETTLE and A. J. P. PIOLT, *J. Chem. Soc. A*, 1968, 1243.

15. J. FUJITA, K. NAKAMOTO and M. KOBAYASHI, *J. Amer. Chem. Soc.*, 1956, **78**, 3295.

16. C. F. SVATOS, D. M. SWEEVY, S. MIZUSHIMA, C. CURRAN and J. V. QUAGLIANO, *J. Amer. Chem. Soc.*, 1957, **79**, 3313.

17. S. MIZUSHIMA, I. NAKAGAWA and J. V. QUAGLIANO, *J. Chem. Phys.*, 1955, **23**, 1367.

18. N. S. GILL, R. H. NOTTOLI and D. W. A. SHARPE, *J. Inorg. Nuclear Chem.*, 1961, **18**, 79.

19. J. K. WILMHURST and H. J. BERUSTEM, *Can. J. Chem.*, 1957, **35**, 1183.

20. A. B. P. LEVER, "Inorganic Electronic Spectroscopy", Elsevier., N. York, 1968, 356.

21. K. C. PATEL, S. R. SRIMALI and D. E. GOLDBORG, *J. Inorg. Nuclear Chem.*, 1975, **37**, 1659.

22. R. H. HOLIM, A. CHAKRAVARTY and L. J. THERIOT, *Inorg. Chem.*, 1966, **5**, 625.

23. A. CHAKRAVARTY and T. S. KAUVAN, *J. Inorg. Nuclear Chem.*, 1967, **29**, 1691.

J. Indian Chem. Soc.,
Vol. LVII, January 1980, pp. 32-34

Binary and Ternary Chelates of Scandium(III), Yttrium(III) and Lanthanum(III) with Ethyleneglycol-*Bis* (β-Aminoethylether)-Tetraacetic Acid as Primary and Substituted Salicylic Acids as Secondary Ligands

ASHOK KUMAR PANDEY, M. CHANDRA, B. V. AGARWALA and A. K. DEY*

Chemical Laboratories, University of Allahabad, Allahabad-211 002

Manuscript received 3 August 1979, accepted 30 December 1979

Formation constants of binary and ternary complexes of the systems of the type : M-L and M-egta-L [M = scandium(III), yttrium(III) and lanthanum(III), egta = ethylene glycol-bis (β-aminoethylether)-tetra acetic acid, L = *o*-cresotic acid (*o*-ca), *m*-cresotic acid (*m*-ca), 5-chlorosalicylic acid (csa), and 3,5-dibromosalicylic acid (dbsa)] have been determined *p*H-metrically at 25° and $\mu = 0.1M$ (KNO_3) in 50% (*v*/*v*) aqueous-ethanol medium. The order of stabilities of ternary complexes have compared with those of corresponding binary complexes, and results discussed on the basis of coulombic interactions.

DUE to the favourable geometry of its donor groups, ethyleneglycol-*bis* (β-aminoethylether) N,N,N,N'-tetraacetic acid (egta) forms stable complexes[1-8] with many metal ions at low *p*H values, but has not been used as a primary ligand in the study of ternary complex formation in solution. The work described here relates to an investigation of ternary complexes of several *tripositive ions* viz., Sc(III), Y(III) and La(III) with egta (as a primary ligand) and *o*-cresotic acid (*o*-ca), *m*-cresotic acid (*m*-ca), 5-chlorosalicylic acid (csa) or 3, 5-dibromosalicylic acid (dbsa) (as secondary ligand) adopting *p*H-metric titration techniques. Under identical conditions the binary complexes of the secondary ligands were also studied for comparison. All the experiments were carried out at 25° and at an ionic strength of 0.1 (KNO_3) *in* 50% (*v*/*v*) aqueous-ethanol medium.

It may mentioned here that the ternary complexes of these secondary ligands with 2, 2'-bipyridine (bipy)[4,5,6], 1,10-phenanthroline (phen)[6] or nitrilotriacetic acid (nta)[7,8] as a primary ligand and several bipositive metal ions have been reported earlier from these laboratories.

Experimental

Solutions and related materials :

Reagents used were of analytical grade. Solutions of nitrates of Sc(III), Y(III) and La(III) were prepared and standardized, and suitable aliquots were diluted and nitric acid added (if necessary) to obtain 0.01 *M* metal(III) nitrate in 0.02 nitric acid. Standard solutions of 0.1 *M* KOH, 0.02 *M* nitric acid and 1.0*M* KNO_3 were prepared as usual[9]. Stock solutions of *o*-ca, *m*-ca, csa and dbsa (0.01 *M* each) in ethanol and an aqueous solution of egta (0.005 *M*) were prepared by direct weighing.

Instrument :

*p*H-measurements were made at 25° using expanded scale *p*H meter (Electronic Corpn. of India) with glass-calomel electrode assembly supplied with the instrument.

Procedure :

(a) *M-L Systems :* Three titration mixtures (total volume 50.0 ml) viz., (a) acid, (b) ligand and (c) chelates were prepared. The concentrations were $N^{\circ} = 0.1$ *M* ; $E^{\circ} = .002$ *M* ; $TC_{L^{\circ}} = 0.001$ *M* ; $TC_{M^{\circ}} = 0.0002$ *M*, symbols having usual meanings (4). Mixtures (a), (b) and (c) were individually titrated against standard alkali and thus three titration curves A, B and C were obtained for each system (figures omitted to economize space).

(b) *M-egta-L Systems* : The following mixtures (total volume 50.0 ml) were prepared (d) 5.0 ml nitric acid (0.02 *M*) + 5.0 ml KNO_3 (1.0 *M*) + 10.0 ml egta (0.005 *M*) + 25.0 ml ethanol ; (e) 5.0 ml metal nitrate (0.01 *M* in 0.02 *M* HNO_3) + 5.0 ml KNO_3 (1.0 *M*) + 10.0 ml egta (0.005 *M*) + 5.0 ml KNO_3 (1.0 *M*) + 10.0 ml egta (0.005 *M*) + 25.0 ml ethanol (f) 5.0 ml HNO_3 (0.02 *M*) + 10.0 ml (0.02 *M*) nitric acid to account for the protons liberated as a result of complexation of egta with metal ion + 5.0 ml KNO_3 (1.0 *M*) + 5.0 ml of secondary ligand (*o*-ca, *m*-ca, csa or dbsa) (0.01 *M*) + 20 ml of ethanol (g) 5.0 ml metal nitrate (0.01 *M* in 0.02 *M* nitric acid) + 5.0 ml KNO_3 (1.0*M*) + 10.0 ml egta (0.005 *M*) + 5.0 ml secondary ligand (*o*-ca, *m*-ca, csa or dbsa) (0.01 *M*) + 20 ml ethanol. The excess acidity in mixture (f) and (g) as compared to (a) was taken into account in the calcula-

* For correspondence.

tions. The mixtures were separately titrated against standard alkali whereby four titrations curves viz., D, E, F and G in each case were obtained (figures omitted).

Calculations :

M-L Systems : The titration curves A, B and C were used to evaluate $\bar{n}_A$ (average number of protons associated with the ligands) ; $\bar{n}$ (average number of ligand molecules attached per metal ion) and pL (free ligand exponent). From these data the proton-ligand and metal-ligand stability constants were obtained (Table 1)[5,6].

TABLE 1—EQUILIBRIUM CONSTANTS IN BINARY AND TERNARY COMPLEXING SYSTEMS ; μ=0.1 (KNO_3) ; 25°

Equilibria	*log equilibrium constant*
L (ligand) = *o*-ca	
$H^+ + L^{2-} \rightleftharpoons LH^-$	12.19±0.09
$LH^- + H^+ \rightleftharpoons LH_2$	4.22±0.08
$Sc^{3+} + L^{2-} \rightleftharpoons ScL^+$	10.11±0.06
$Y^{3+} + L^{2-} \rightleftharpoons YL^+$	9.43±0.02
$La^{3+} + L^{2-} \rightleftharpoons LaL^+$	8.26±0.05
$[Sc(egta)]^- + L^{2-} \rightleftharpoons [Sc(egta)L]^{3-}$	5.72±0.01
$[Y(egta)]^- + L^{2-} \rightleftharpoons [Y(egta)L]^{3-}$	5.59±0.01
$[La(egta)]^- + L^{2-} \rightleftharpoons [La(egta)L]^{3-}$	5.42±0.02
L = *m*-ca	
$H^+ + L^{2-} \rightleftharpoons LH^-$	12.29±0.04
$LH^- + H^+ \rightleftharpoons LH_2$	4.10±0.07
$Sc^{3+} + L^{2-} \rightleftharpoons ScL^+$	10.41±0.04
$Y^{3+} + L^{2-} \rightleftharpoons YL^+$	9.65±0.05
$La^{3+} + L^{2-} \rightleftharpoons LaL^+$	8.63±0.03
$[Sc(egta)]^- + L^{2-} \rightleftharpoons [Sc(egta)L]^{3-}$	5.83±0.01
$[Y(egta)]^- + L^{2-} \rightleftharpoons [Y(egta)L]^{3-}$	5.70±0.01
$[La(egta)]^- + L^{2-} \rightleftharpoons [La(egta)L]^{3-}$	5.49±0.02
L = csa	
$H^+ + L^{2-} \rightleftharpoons LH^-$	11.56±0.09
$LH^- + H^+ \rightleftharpoons LH_2$	3.11±0.05
$Sc^{3+} + L^{2-} \rightleftharpoons ScL^+$	9.07±0.03
$Y^{3+} + L^{2-} \rightleftharpoons YL^+$	8.48±0.03
$La^{3+} + L^{2-} \rightleftharpoons LaL^+$	7.75±0.03
$[Sc(egta)]^- + L^{2-} \rightleftharpoons [Sc(egta)L]^{3-}$	5.21±0.02
$[Y(egta)]^- + L^{2-} \rightleftharpoons [Y(egta)L]^{3-}$	5.06±0.02
$[La(egta)]^- + L^{2-} \rightleftharpoons [La(egta)L]^{3-}$	4.86±0.01
L = dbsa	
$H^+ + L^{2-} \rightleftharpoons LH^-$	12.05±0.06
$LH^- + H^+ \rightleftharpoons LH_2$	2.86±0.03
$Sc^{3+} + L^{2-} \rightleftharpoons ScL^+$	9.68±0.01
$Y^{3+} + L^{2-} \rightleftharpoons YL^+$	8.84±0.07
$La^{3+} + L^{2-} \rightleftharpoons LaL^+$	8.20±0.07
$[Sc(egta)]^- + L^{2-} \rightleftharpoons [Sc(egta)L]^{3-}$	5.54±0.02
$[Y(egta)]^- + L^{2-} \rightleftharpoons [Y(egta)L]^{3-}$	5.49±0.01
$[La(egta)]^- + L^{2-} \rightleftharpoons [La(egta)L]^{3-}$	5.29±0.01

The absence of polynuclear species etc was confirmed by repeating the experiments using several concentrations of the reactants, when the results obtained were identical.

M-egta-L Systems : It is observed that complete formation of $(M\text{-}egta)^-$ species occurs at a $pH \simeq 4$, which remains stable even at higher pH values. Thus, the horizontal distance between curves (F) and (G) were measured and used for calculation of $\bar{n}_{mix}$, average number of secondary ligand molecules attached per $(M\text{-}egta)^-$, as described earlier[6]. From the values of $\bar{n}_{mix}$ so obtained, the values for free ligand exponent pL_{mix} were evaluated[6].

The parameters $\bar{n}_{mix}$ and pL_{mix} were treated similarly as in the binary systems to obtain formation constants corresponding to mixed ligand complexes formed (Table 1).

Results and Discussion

Binary complexing systems :

The values of proton-ligand stability constants obtained by average value method (Table 1) are in agreement with those reported earlier[5,6].

Only 1 : 1 binary chelates of Sc(III), Y(III) and La(III) could be studied with the ligands viz., *o*-ca, *m*-ca, csa and dbsa. Studies beyond 1 : 1 stage could not be carried out because of occurence of opacity/turbidity/precipitation.

The stability order of metal chelates with respect to various ligands are : *m*-ca>*o*-ca>dbsa>csa. While those with respect to metal ions are Sc(III)>Y(III)>La(III).

Ternary complexing systems :

The values of log $K^{M\text{-}egta}_{M\text{-}egta\text{-}L}$ [$K^{M\text{-}egta}_{M\text{-}egta\text{-}L}$ = mixed ligand formation constant in M-egta-L systems] is less than log K_1[K_1 = first step formation constant of binary complexes of the secondary ligands]. This behaviour can be explained out the basis of coulombic interactions between various ligand anion species present. In the mixed ligand complex formation there is a repulsion between two negative charges from the secondary ligand anion and four negative charges from egta anion. During the formation of ML species this type of repulsion is absent, which justifies log K_1 > log $K^{M\text{-}egta}_{M\text{-}egta\text{-}L}$. The stability order with respect to metal ions and the ligands follow the same pattern as those in binary complexing systems.

Acknowledgement

The financial support from Council of Scientific and Industrial Research, New Delhi, is gratefully acknowledged.

References

1. G. SCHWARZENBACH, H. SENN and G. ANDEREGG, *Helv. Chim. Acta*, 1957, **40**, 1886.

2. H. J. Holloway and C. N. Reilley, *Anal. Chem.*, 1960, **32**, 249.

3. K. H. Schroder, *Acta. Chem. Scand.*, 1963, 17, 1509.

4. K. Dwivedi, B. K. Agarwal, M. Chandra and A. K. Dey, *J. Indian Chem. Soc.*, 1977, **54**, 474.

5. K. Dwivedi, M. Chandra and A. K. Dey, *Transition Metal Chem.*, 1977, **2**, 186.

6. B. K. Agrawal, M. Chandra, B. V. Agarwala and A. K. Dey, *Indian J. Chem.*, 1978, **16A**, 840.

7. B. K. Agrawal, M. Chandra, B. V. Agarwala and A. K. Dey, *Indian J. Chem.*, 1977, **15A**, 632; *J. Indian Chem. Soc.*, 1977, **54**, 981.

8. R. K. Mittal, M. Chandra and A. K. Dey, *Monatsh. Chem.*, 1978, **309**, 858, 958.

9. L. G. Sillén, Some Laboratory Methods, KTH Stockholm, 1959.

J. Indian Chem. Soc.,
Vol. LVII, January 1980, pp. 35-38

Metal Complexes with Sulphur Donor Ligands-I. Preparation and Characterisation of Some Mixed Ligand Complexes Containing Bidentate Tertiary Amines and Ethyl Xanthate

W. U. MALIK, R. BEMBI and V. K. BHARDWAJ

Department of Chemistry, University of Roorkee, Roorkee

Manuscript received 18 September 1979, accepted 30 November 1979

Mixed ligand complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) containing ethyl xanthate and 1,10 phenanthroline or 2, 2′ bipyridyl have been prepared through a two step process. In the first step $[M(LN_2)(H_2O)_4]^{2+}$ is prepared which in the second step on interaction with ethylxanthate results in the replacement of the four water molecules by two xanthate molecules. The composition of the complexes has been determined by radiometric, amperometric and potentiometric titrations and by chemical analysis of the isolated complexes. Infrared spectra show the binding of the xanthate and 1,10 phenanthroline or 2, 2′ bipyridyl to the metal.

THE increasing commercial value of transition metal complexes of xanthates and dithiocarbamates has aroused considerable interest in their chemistry. While their analytical applications are well known[1-3], they are now finding extensive use in vulcanisation of rubber, froth floatation process for concentration of sulphide ores, as antioxidants, lubricants[4-7] and have been found to possess fungicidal and insecticidal activity[8]. Although a large amount of work has been carried out on the simple metal xanthates, little attention has been paid to their mixed ligand complexes inspite of the fact that introduction of another ligand generally increases their fungicidal and insecticidal activity to a considerable extent. An attempt has thus been made to prepare some mixed ligand complexes of ethyl xanthate and 1,10 phenanthroline (phen) or 2,2′ bipyridyl (bipy).

Experimental

Reagent grade (S. Merck) 1,10 phenanthroline, 2,2' bipyridyl and potassium ethyl xanthate were used as received without any further purification. The metals were reagent grade BDH products.

Preparation of the complexes :

In order to prepare the desired complexes, a two step process was adopted. In the first step, the metal complexes with 1,10 phenanthroline and 2,2′ bipyridyl of the type $[M(LN_2)(H_2O)_4]^{2+}$ were prepared by the method adopted by Parikh and Bhattacharya[9] (LN_2 denotes phen or bipy). In the first step, in a typical preparation of the copper complex, a mixture of 2 mM of 1,10 phenanthroline in 10 cm^3 of ethanol and 2 mM of $CuCl_2$ in 10 cm^3 of water was refluxed for about 45 min on a water bath. On cooling and adding excess of absolute ethyl alcohol, a green complex was precipitated which was suction filtered and washed with ice-cold 50% ethanol. The crude product was dissolved in a minimum quantity of hot 50% ethanol and recrystallised by slow cooling to 0° followed by addition of excess absolute ethanol. The product was dried under vacuum over anhydrous calcium chloride. Analysis of the dried product corresponded to $[Cu(phen)(H_2O)_4]Cl_2$. Similarly complexes were prepared from $ZnSO_4$, $CdSO_4$, $NiSO_4$, $MnSO_4$ and $CoSO_4$ and 2,2′ bipyridyl.

In the second step, 1 mM of the above complex was dissolved in 10 cm^3 of water and to this 20 cm^3 of an aqueous solution containing 2 mM of potassium ethyl xanthate was added dropwise with magnetic stirring. A brick red precipitate of $[Cu(phen)(xan)_2]$ was obtained which was suction filtered, washed with 20% ethanol followed by ether and dried in vacuum.

Composition of the complexes :

The composition of the complexes was determined by amperometric, potentiometric and radiometric titrations.

Amperometric titrations in 0.1*M* K_2SO_4 were carried out at potentials lying either on the plateaux of the polarograms of potassium ethyl xanthate or the complex $[M(LN_2)(H_2O)_4]^{2+}$. 0.005% gelatin was used as maxima suppressor in the case of copper-bipyridyl-xanthate complex only. Nitrogen was bubbled through the solutions in the polarographic cell for about 15 min before commencing the titration and then for 5 min after each addition of the titrant. Current was then measured after allowing the solution to stand for 2 minutes. The current was measured with Toshniwal manual

polarograph (type CLO-2A) used in conjunction with a Pye scalamp galvanometer. The capillary characteristic was found to be 1.77 $mg^{2/3}s^{-1/2}$.

Potentiometric titrations were carried out by taking 40 cm^3 of 0.002M of potassium ethyl xanthate solution in the cell and titrating against 0.02M $[M(LN_2)(H_2O)_4]^{2+}$. In the case of $[Cd(phen)(H_2O)_4]^{2+}$ a solution of 0.001M xanthate was titrated against 0.01M $[Cd(phen)(H_2O)_4]^{2+}$. The solutions were magnetically stirred for 1 min after each addition of the titrant and allowed to stand for 2 min before recording the potential. The potential was further checked twice after an interval of 1 min each. Reverse titrations were not successful and gave erratic results. For determining the inflection points, both the first derivative ($\triangle E/\triangle V$) and the second derivative ($\triangle^2 E/\triangle V^2$) were plotted against the volume of the titrant. The potential was measured using a Toshniwal portable potentiometer using an external galvanometer with a lamp and scale arrangement. A silver-silver sulphide electrode and a saturated calomel electrode were used as indicator and reference electrodes respectively. The silver-silver sulphide electrode was prepared as described[11].

Radiometric titrations were carried out by preparing labelled $[M^*(LN_2)(H_2O)_4]^{2+}$ using radioisotopes of cobalt, zinc, manganese and cadmium and titrating against potassium ethyl xanthate. Both direct and reverse titrations were carried out using a concentration of about 0.02M of the reagents as previously described[10]. Radioisotopes, Co^{58}, Zn^{65}, Mn^{54} and Cd^{115m} as carrier free samples were obtained from the Bhabha Atomic Research Establishment, Trombay, India in the form of their chlorides in HCl solution (activity 0.5 to 2.0 mCi/ml). 0.2 to 1.0 cm^3 of the active sample was diluted to 30 cm^3 with the inactive solution (0.2 M) of the same metal ion, which was then used to prepare $[M^*(LN_2)(H_2O)_4]^{2+}$. The activity of the solutions was measured with a γ-ray scintillation spectrometer employing a NaI(Tl) crystal. In the case of the cadmium complex the activity was measured using a Geiger Muller counter since Cd^{115m} is a β-emitter.

Chemical analysis :

The metal content of the complexes was determined after decomposing the sample by prolonged boiling with concentrated nitric acid. Excess HNO_3 was removed by slow heating after adding a few drops of conc. H_2SO_4. The solution was cooled, diluted to about 20 cm^3 with distilled water and made up to 100 cm^3 after transferring to a measuring flask. Manganese was estimated as permanganate after oxidation with periodate, nickel with dimethyl glyoxime and copper with diethyldithiocarbamate spectrophotometrically[12]. Zinc, cadmium and cobalt were estimated gravimetrically with dihydrogen ammonium phosphate and α-nitroso β-naphthol respectively[12]. For spectrophotometric determinations, about 20 mg of the sample was used while for the gravimetric estimation, about 200 mg was taken.

Sulphur content of the complexes was determined after decomposing about 200 mg of the compound by refluxing for about 4 h with 0.5 g of KOH and 1.5 g of $KMnO_4$ in 100 ml of H_2O whereby the sulphur content of the complex was converted to $SO_4^=$. The sulphate ions were estimated gravimetrically after precipitation as $BaSO_4$ with $BaCl_2$.

Carbon and nitrogen were estimated by the standard microanalytical methods.

Infrared spectra :

Infrared spectra of the complexes in the range 4000-240 cm^{-1} were recorded on a Beckmann IR 20 spectrophotometer. The infrared spectra in the range 600-240 cm^{-1} were obtained as nujol mulls on polyethylene plates and in the range 4000-600 cm^{-1} in KBr pellets.

Results and Discussion

Preliminary studies show that xanthate on interaction with the complex $[M(LN_2)(H_2O)_4]^{2+}$ replaces the four water molecules of the complex to give $[M(LN_2)(xan)_2]$. These observations find support from the results of amperometric, potentiometric and radiometric titrations.

In the direct radiometric titrations (with potassium ethyl xanthate as titrant), the activity

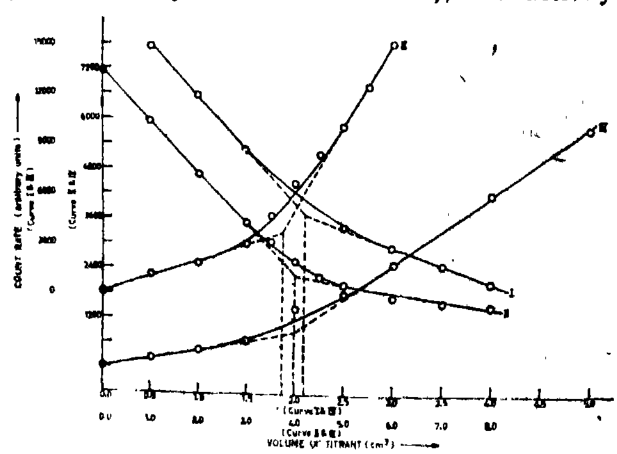


Fig. 1. Radiometric titrations.
(a) Direct titration :
(I) 4.0 cm^3 of 0.02$M$$[Mn(Phen)(H_2O)_4]SO_4$ against 0.08M Xanthate.
(II) 2.0 cm^3 of 0.02$M$$[Co(Bipy)(H_2O)_4]SO_4$ against 0.02M Xanthate
(b) Reverse titration :
(III) 2.0 cm^3 of 0.08M Xanthate against 0.02$M$$[Mn(Phen)(H_2O)_4]SO_4$
(IV) 4.0 cm^3 of 0.02M Xanthate against 0.02$M$$[Co(Bipy)(H_2O)_4]SO_4$

shows a continuous decrease. The rate of decrease is rapid in the beginning and shows a fall as the titration proceeds. The inflection point (Typical curves, Fig. 1) corresponds to the complete substitution of the four water molecules by two xanthate molecules. In the reverse titrations (with the active metal complex $[M^{*}(LN_2)(H_2O)_4]^{2+}$ as titrant) the activity shows a slow increase in the beginning and then a rapid increase in activity as the titration proceeds (Typical curves, Fig. 1). The inflection point corresponds to the formation of a 1 : 2 complex. Since only one inflection point is observed in both the direct and reverse titrations corresponding to a 1 : 2 complex, the four water molecules of $[M(LN_2)(H_2O)_4]^{2+}$ are replaced either simultaneously by two xanthate molecules or the complex $[M(LN_2)(xan)(H_2O)_2]^{+}$ if formed is very unstable and reacts very rapidly with another xanthate molecule to give the final product. The continuous increase or decrease is activity points towards a reversible reaction between the complex $[M(LN_2)(H_2O)_4]^{2+}$ and xanthate represented by the following equation :

$$[M(LN_2)(H_2O)_4]^{2+} + 2xan^- \rightleftharpoons [M(LN_2)(xan)_2] + 4H_2O$$

Radiometric titrations with the Ni(II) and Cu(II) complexes could not be carried out due to the lack of their isotopes.

Amperometric titrations (both direct and reverse) show the formation of only 1 : 2 complexes (Typical curves, Fig. 2). The continuous increase or decrease in the current support the above mentioned reversible reaction.

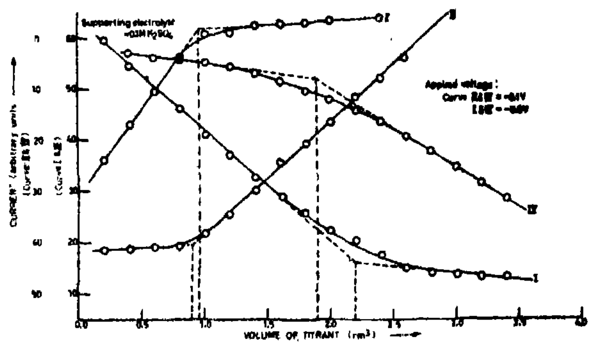


Fig. 2. Amperometric titrations.
(a) Direct titrations :
(I) 10.0 cm³ of 0.001M[Cu(Phen)$(H_2O)_4$]Cl_2 against 0.01M Xanthate
(II) 20.0 cm³ of 0.002M Xanthate against 0.02M[Co(Bipy)$(H_2O)_4$]SO_4
(b) Reverse titrations :
(III) 20.0 cm³ of 0.001M Xanthate against 0.01M [Cu(Phen)$(H_2O)_4$]Cl_2
(IV) 10.0 cm³ of 0.002M [Co(Bipy)$(H_2O)_4$]SO_4 against 0.02M Xanthate

Potentiometric titrations also show the formation of 1 : 2 complexes (Typical curves, Fig. 3). These studies further show that a silver-silver sulphide electrode can be successfully used to monitor the activity of sulphur containing ligands like xanthates and dithiocarbamates.

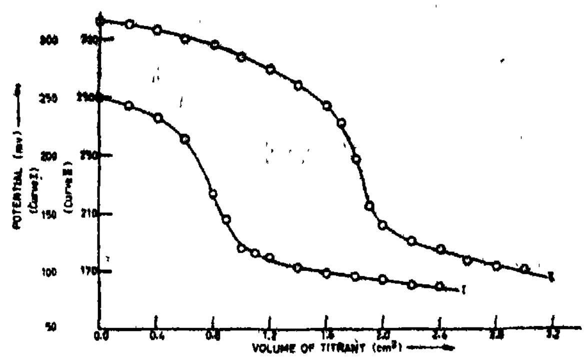
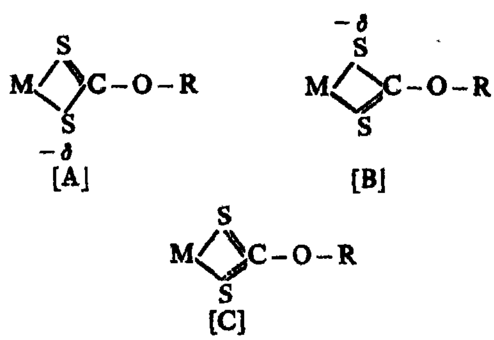


Fig. 3. Potentiometric tetrations.
(I) 20.0 cm³ of 0.001M Xanthate against 0.01M[Cd(Phen)$(H_2O)_4$]SO_4
(II) 40.0 cm³ of 0.002M Xanthate against 0.02M[Cd(Bipy)$(H_2O)_4$]SO_4

Chemical analysis of the isolated products (Table 1) corresponds to the composition $[M(LN_2)(xan)_2]$, where M = Cu(II), Ni(II), Zn(II), Cd(II), Mn(II) or Co(II), which confirms the results obtained above.

Infrared spectral data show the coordination of the metal to xanthate and 1,10 phenanthroline or 2,2' bipyridyl. The (M – N) band[16] for the complexes with Co(II) and Cd(II) appears between 320 and 340 cm^{-1} while with Mn(II), Ni(II), Cu(II) and Zn(II) the band[15,16] is observed between 250-300 cm^{-1}. The other ring stretching vibrations of the ligand LN_2 appearing in the range of 1600-1400 cm^{-1} confirm the presence of this ligand in the complexes.

Potassium ethyl xanthate is also a bidentate ligand and binds through both its sulphur atoms. Three canonical forms of the xanthate complex can be visualised[1], viz.,



The infrared spectra does not show any band which can be assigned exclusively to a C=S fre-

TABLE 1—CHEMICAL ANALYSIS OF THE COMPLEXES

Complex	%metal		%S		%C		%N	
	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
$[Mn(phen)(xan)_2]$	11.4	11.5	26.6	26.9	45.4	45.8	5.6	5.9
$[Mn(bipy)(xan)_2]$	12.0	12.1	28.2	28.3	42.6	42.4	6.1	6.2
$[Co(phen)(xan)_2]$	12.3	12.2	26.5	26.6	44.8	44.9	5.9	5.8
$[Co(bipy)(xan)_2]$	12.7	12.9	28.2	28.0	42.1	42.0	6.0	6.1
$[Ni(phen)(xan)_2]$	12.2	12.3	26.3	26.2	45.0	44.9	5.8	5.9
$[Ni(bipy)(xan)_2]$	12.9	12.8	27.8	28.0	42.1	42.0	6.3	6.1
$[Cu(phen)(xan)_2]$	13.2	13.1	26.2	26.4	44.4	44.5	5.6	5.8
$[Cu(bipy)(xan)_2]$	13.7	13.8	27.9	27.6	41.8	41.6	6.2	6.1
$[Zn(phen)(xan)_2]$	13.5	13.4	26.8	26.4	44.0	44.2	5.8	5.7
$[Zn(bipy)(xan)_2]$	14.3	14.1	27.8	27.6	40.4	40.5	6.2	6.0
$[Cd(phen)(xan)_2]$	21.2	21.0	23.8	24.0	40.6	[illegible].4	5.2	5.3
$[Cd(bipy)(xan)_2]$	21.8	22.0	25.4	25.1	37.8	37.6	5.8	5.5

quency. Further, the spectra shows bands in the 1120 cm^{-1}, 810 cm^{-1} and 620 cm^{-1} regions which can be assigned to the (C–S) absorptions[17,18] while the (C–O) frequency[18-20] appears in the 1250 cm^{-1} region. It is thus feasible to assume that the canonical form [C] makes a significant contribution to the overall structure. The (M–S) absorption[18,21] appearing in the 390 cm^{-1} region confirms the bonding of the xanthate through its sulphur atom to the metal.

References

1. R. J. MAGEE, *Revs. Anal. Chem.*, 1973, **1**, 333.
2. J. BULANDR, M. DOLEZIL and J. PETROVICKY, *Chem. Listy*. 1963, **57**, 808.
3. M. DELEPHINE, *Bull. Soc. Chim. France*, 1958, 5.
4. J. W. WARK and A. B. COX, *Trans. Amer. I.M.M.E.*, 1946, **134**, 64.
5. C. H. G. BUSHELL and M. MOLNARICH, *Trans. Amer. I.M.M.E.*, 1954, **205**, 734.
6. D. COUCOUVANIS, *Prog. Inorg. Chem.*, 1970, **11**, 233.
7. R. EISENBERG, *Prog. Inorg. Chem.*, 1970, **12**, 295.
8. G. J. M. VANDERKERK and H. L. KLOPPING, *Rec. Trav. Chim.*, 1952, **71**, 1179, *Nature*, 1955, **176**, 308.
9. P. C. PARIKH and P. K. BHATTACHARYA, *J. Indian Chem. Soc.*, 1076, **53**, 776.
10. W. U. MALIK, B. P. SINGH and J. P. JAIN, *J. Radioanal. Chem.*, 1972, **12**, 553.
11. M. M. KHAN and A. U. MALIK, *J. Electroanal Chem.*, 1971, **29**, 421.
12. A. I. VOGEL, 'A Text Book of Quantitative Inorganic Analysis', Longmans, London, 1968.
13. K. NAKAMOTO, 'Infrared and Raman Spectra of Inorganic and Coordination Compound', John Wiley, New York, 1979.
14. B. HUTCHINSON, J. TAKEMOTO and K. NAKAMOTO, *J. Amer. Chem. Soc.*, 1972, **92**, 3335.
15. V. SAITO, J. TAKEMOTO, B. HUTCHINSON and K. NAKAMOTO, *Inorg. Chem.*, 1972, **11**, 2003.
16. J. TAKEMOTO, B. HUTCHINSON and K. NAKAMOTO, *Chem. Commun.*, 1971, 1007.
17. K. NAKAMOTO, J. FUJITA, R. A. CONDRATE and Y. MORIMOTO, *J. Chem. Phys.*, 1963, **39**, 423.
18. G. W. WATT and B. J. McCORMICK, *Spectrochim. Acta*, 1965, **21**, 753.
19. M. L. SHANKARANARAYAN and C. C. PATEL, *Canad. J. Chem.*, 1961, 39, 1633.
20. L. H. LITTLE, G. W. POLING and J. LEJA, *Canad. J. Chem.*, 1961, **39**, 745.
21. R. A. WINOGRAD, D. J. LEWIS and S. J. LIPPARD, *Inorg. Chem.*, 1975, **14**, 2601.

J. Indian Chem. Soc.,
Vol. LVII, January 1980, pp. 39-41

Metal Chelates of Some N-Acyl Hydroxamic Acids Containing Sulphonimido Group. Part I : *p*H-Metric Study of the Complex Formation of Cu(II) with N(N-Benzene Sulphonyl Glycyl) N-Phenyl Hydroxyl Amine

G. N. MUKHERJEE*

Department of Pure Chemistry, Inorganic Chemistry Laboratory, University College of Science, 92, Acharya Prafulla Chandra Road, Calcutta-700 009

and

M. M. GHOSH

Department of Chemistry, Charu Chandra College, 22, Lake Road, Calcutta-700 029

Manuscript received 14 September 1979, accepted 30 November 1979

pH-metric study of the reaction of Cu(II) with the ligand N(N′-benzenesulphonyl glycyl) N-phenyl hydroxyl amine, $C_6H_5SO_2NHCH_2CON(OH)C_6H_5$, indicated the formation of 1 : 1 and 1 : 2 metal ligand complexes. Stepwise stability constants (K_1 and K_2) and successive acid dissociation constants (k_{2NH} and k_{1NH}) of the 1 : 2 complex have been determined by following the procedure of Irving and Rossotti. Log K_1, log K_2, pk_{2NH} and pk_{1NH} are found to be 8.19 ± 0.03, 6.71 ± 0.03, 10.30 ± 0.04 and 11.00 ± 0.04 respectively at $30\pm0.5°$ in 50% (v/v) water-dioxan medium at ionic strength 0.50 *M* ($NaClO_4$). The pk_2 and pk_1 values of the ligand are 9.94 ± 0.03 and 11.72 ± 0.04 respectively under identical condition. Unusually small enhancement of acidity of the imido (– NH –) group on coordination to Cu(II) has been explained.

DURING the last four decades several N-acyl hydroxamic acids have been proved very useful for the determination of quite a large number of metal ions and separation of many difficulty separable mixtures[1]. Incorporation of a sulphonimido (– SO_2NH –) group in suitable positions of acyl hydroxamic acids has produced an interesting series of chelating agents with one more donor site having some specificity for the metal ions of group IB and IIB[2-5]. The present communication describes the isolation and characterisation of the ligand, N(N′-benzenesulphonyl glycyl) N-phenylhydroxyl amine, $C_6H_5SO_2NHCH_2CON(OH)C_6H_5$(or LH_2) and pH-metric study of its acid dissociation and complex formation with Cu(II) at $30\pm0.5°$ in 50% (v/v) water-dioxan medium at a constant ionic strength, $\mu=0.50$ *M*($NaClO_4$).

Experimental

The ligand N(N′-benzenesulphonyl glycyl) N-phenyl hydroxyl amine was obtained as a white solid on condensing N-benzenesulphonyl glycyl chloride with β-phenyl hydroxyl amine in aqueous solution in the presence of $NaHCO_3$, followed by neutralisation with dil. H_2SO_4 to pH=4.0. It was purified by recrystallisation from aqueous ethanol, dried in a vacuum desiccator over conc. H_2SO_4 and KOH (solid) and analysed. Found, m.p. 141-142° ; C, 55.56 ; H, 5.01 ; N, 9.08%. Calc. for $C_6H_5SO_2NHCH_2CON(OH)C_6H_5$: C, 54.90 ; H, 4.58 and N, 9.15%. IR(KBr)[6] : OH 3265(m), NH 3190(m), C=O 1635(s), -SO_2N< 1335(s), 1165(s), cm^{-1} and UV : $\lambda_{max}^{Ethanol}$ 252 and 224 nm (log ϵ 4.07 and 3.97 respectively). All other reagents were either of A.R. quality or properly purified and their solutions were prepared in CO_2-free water and purified dioxan[7].

pH-metric titrations of 50 ml solutions containing (i) 0.01(*M*) $HClO_4$, (ii) 0.01(*M*) $HClO_4$+0.01(*M*) LH_2, (iii) 0.01(*M*) $HClO_4$+0.01(*M*) LH_2+0.002(*M*) Cu(II), (iv) 0.01(*M*) $HClO_4$+0.01(*M*) LH_2+0.003(*M*) Cu(II)

were performed in 50% (v/v) water-dioxan medium with a standard solution of NaOH in the same solvent mixture while maintaining the ionic strength constant at $\mu=0.50$(*M*) by adding requisite amount of $NaClO_4$.

pH-measurements were made with a Cambridge pH-meter (Portable type) using a glass electrode of 1-13 pH range and a saturated calomel electrode, connected to the cell by means of an agar-2(*M*) $NaNO_3$ bridge. The meter was calibrated with aqueous buffer solutions, e. g., 0.01(*M*) $HClO_4$, phthalate buffer and borate buffer solutions with appropriate temperature corrections.

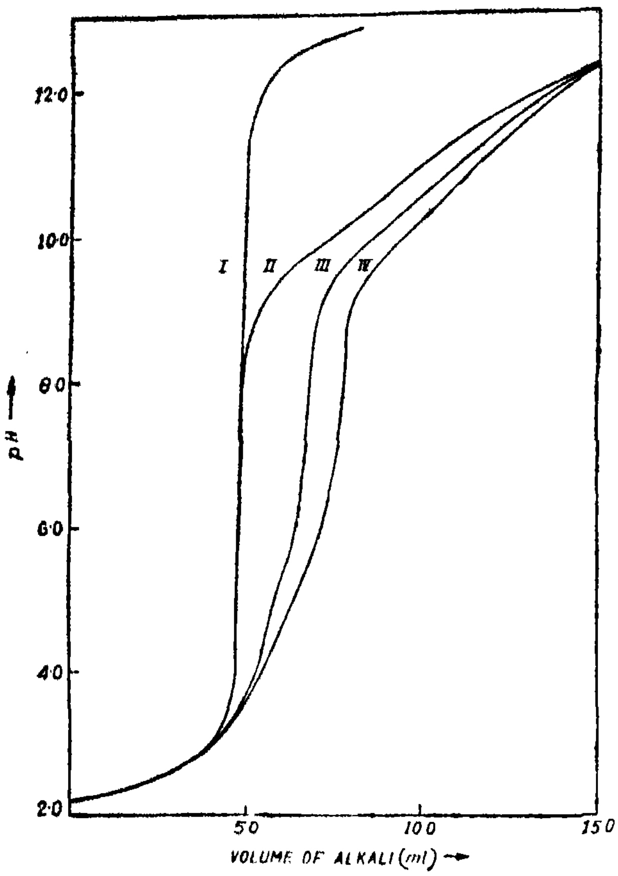


Fig. 1. pH-titration Curves :

Curve I : 0.01(*M*) $HClO_4$
" II : 0.01(*M*) $HClO_4$+0.01(*M*) LH_2
" III : 0.01(*M*) $HClO_4$+0.01(*M*) LH_2+0.002(*M*) Cu(II)
" IV : 0.01(*M*) $HClO_4$+0.01(*M*) LH_2+0.003(*M*) Cu(II)

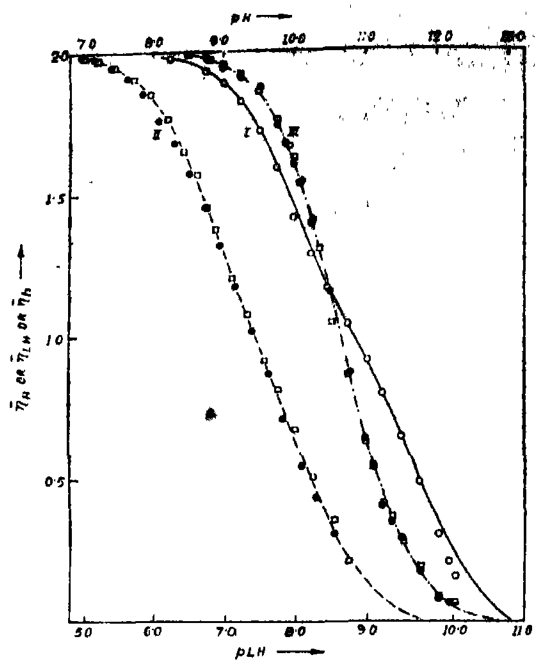


Fig. 2. Complex formation Curves :

Curve I : ○—○, $\bar{n}_H$ (pH) plot for LH_2.
" II : $\bar{n}_{LH}$ (pLH) plot for $[Cu(LH)_2]$:
●—●, 0.002(*M*) Cu(II) ;
□—□, 0.003(*M*) Cu(II).
" III : $\bar{n}_H$ (pH) plot for $[Cu(LH)_2]$:
●—●, 0.002(*M*) Cu(II) and
□—□, 0.003(*M*) Cu(II).

*p*H-titration curves, (*p*H vs. volume of standard NaOH solution) were drawn (Fig. 1) and the average coordination numbers ($\bar{n}$ values) and free ligand concentrations were calculated by following the procedure of Irving and Rossotti[8].

Results and Discussion

I. *Stepwise Acid Dissociation of the Ligand,* LH_2 :

Consumption of two equivalents of alkali per mole of the ligand, LH_2, in solution (ii) in the *p*H range 8.5 to 12.5 (Curve II, Fig. 1) indicated two steps of acid dissociation for LH_2 as represented by :

$$LH_2 \overset{k_2}{\rightleftharpoons} H^+ + LH^- \qquad \dots \dots \quad (1)$$

$$LH^- \overset{k_1}{\rightleftharpoons} H^+ + L^{2-} \qquad \dots \dots \quad (2)$$

where k_1 and k_2 are the two successive proton-ligand (L^{2-}) instability constants. The plot of $\bar{n}_H$ (the average number of protons bound to the ligand ion, L^{2-}) against *p*H (Curve I, Fig. 2) shows $k_2/k_1 < 100$. The refined values of the constants were evaluated by the method of linear plots employing suitable forms of the function

$$\bar{n}_H = \frac{\left(\frac{2[H^+]^2}{k_1 k_2} + \frac{[H^+]}{k_1}\right)}{\left(\frac{[H^+]^2}{k_1 k_2} + \frac{[H^+]}{k_1} + 1\right)} \qquad \dots \dots \quad (3)$$

The refined pk_2 and pk_1 values are stated in Table 1.

II. *Complex formation of Cu(II) with* LH_2 :

*p*H-titration curves of solutions (iii) and (iv) (Curves III and IV, Fig. 1) shows that two equivalents of acid per gm ion of Cu(II) were liberated in the *p*H range 3.0 to 7.0. From an analysis of the titration data in this *p*H range according to the procedure of Irving and Rossotti[8] it was found that one equivalent of acid per gm ion of Cu(II) was liberated for the association of each mole of the ligand species to the Cu(II) ion. Stepwise complex formation of Cu(II) with LH_2 has, therefore, been assumed to take place according to (4) and (5) :

$$Cu^{2+} + LH_2 \overset{K_1}{\rightleftharpoons} [Cu(LH)^+] + H^+ \qquad \dots \dots \quad (4)$$

$$[Cu(LH)^+] + LH_2 \overset{K_2}{\rightleftharpoons} [Cu(LH)_2] + H^+ \qquad \dots \quad (5)$$

where, K_1 and K_2 are the two successive formation constants. From the complex formation curves, $\bar{n}_{LH}$ (pLH), (Curve II, Fig. 2) it appears that the steps (4) and (5) are overlapping (e.g., $K_1/K_2 < 100$). The log K_1 and log K_2 values were evaluated by projection strip method[9a] and finally refined by the method of linear plots using suitable forms of the function :

$$\bar{n}_{LH} = (K_1[LH] + 2K_1K_2[LH]^2)/(1 + K_1[LH] + K_1K_2[LH]^2) \quad \ldots (6)$$

The refined values of log K_1 and log K_2 are stated in Table 1.

TABLE 1—PROTON-LIGAND AND Cu(II)-LIGAND STABILITY CONSTANTS AT 30±0.5°C IN 50% (v/v) WATER-DIOXAN MEDIUM HAVING IONIC STRENGTH 0.50M ($NaClO_4$)

pk_2	pk_1	log K_1	log K_2	pk_{2NH}	pk_{1NH}
9.94 ±0.03	11.72 ±0.04	8.19 ±0.03	6.71 ±0.03	10.30 ±0.04	11.00 ±0.04

III. *Acid dissociation of the Complex [Cu(LH)₂] :*

Liberation of two further moles of acid from solutions (iii) and (iv) in the pH range from 9.0 to 12.1 (Curves III and IV, Fig. 1) i.e., after the association of two moles of the ligand ion, LH^-, per mole of copper, was accounted for by assuming stepwise deprotonation of the complex, $[Cu(LH)_2]$, evidently from the coordinated sulphonimido $-SO_2NH-$ groups :

$$[Cu(LH)_2] \overset{k_{2NH}}{\rightleftharpoons} [Cu(L)(LH)]^- + H^+ \quad \ldots \quad \ldots (7)$$

$$[Cu(L)(LH)]^- \overset{k_{1NH}}{\rightleftharpoons} [Cu(L)_2]^{2-} + H^+ \quad \ldots \quad \ldots (8)$$

where k_{2NH} and k_{1NH} are the two successive acid dissociation constants. The values of $\bar{n}_h$, the average number of protons bound to the complex ion $Cu(L)_2^{2-}$, were calculated assuming all the Cu(II) ion in the form of the 1 : 2 complex at pH values greater than 9.0. The $\bar{n}_h$ (pH) plot, (Curve III, Fig. 2) shows that the steps (7) and (8) are overlapping (e.g., $k_2^{NH}/k_{1NH} < 10$). Therefore, as in the case of K_1 and K_2 the constants k_{2NH} and k_{1NH} were also evaluated by projection strip method[9a] and finally refined by the method of linear plots employing suitable forms of the function similar to (3) with $\bar{n}_H$, k_2 and k_1 replaced by $\bar{n}_h$, k_{2NH} and k_{1NH} respectively. The refined values of pk_{2NH} and pk_{1NH} are stated in Table 1.

Limits of error in the determination of the constants were found out as usual[9b] and are stated in Table 1. Standard deviations[9b] were found to be in the range ±0.015 – ±0.025.

Unlike the sulphonimides of the amino acids[2-5] the enhancement of acidity of the imido (–NH–) group on coordination to a metal ion has been found to be small in the present case. X-ray study on the crystalline complex, $Cu(LH)_2 . 2H_2O$[10] indicates that copper is coordinated through oxygens of the —C(=O)—N(—O)— moity in the basal plane of the copper coordination sphere. These two observations suggest that the nitrogens (i.e., of the –NH– group) most probably occupy the apical positions about copper and the smaller enhancement of acidity of the imido group reflect a Z-out John-Teller distortion, characteristic of Cu(II) and thereby weakening the Cu–N bonds.

Acknowledgement

Authors' sincerest thanks are due to Professor N. N. Ghosh, Retired Professor of Chemistry, Calcutta University for his interest in the work, Mr. V. Mani of Saha Institute of Nuclear Physics, Calcutta for taking interest in the X-ray study and to Mr. J. C. Ghosh of this department for IR spectra.

References

1. D. C. BHURA, *Technical News Service*, **5**, No. 3 and 4 (1973) and references therein.
2. N. N. GHOSH and M. N. MAZUMDER, *J. Indian Chem. Soc.*, 1963, **40**, 945 ; 1967, **44**, 115, 559.
3. N. N. GHOSH and M. DASGUPTA, *J. Indian Chem. Soc.*, 1966, **43**, 545 , 1971, **48**, 15 ; *Z. anorg. allg. Chem.*, 1970, **375**, 815.
4. N. N. GHOSH and A. BHATTACHARYYA, *J. Indian Chem. Soc.*, 1969, **46**, 1040 ; 1971, **48**, 889 ; *J. Inorg. Nuclear Chem.*, 1973, **35**, 517.
5. N. N. GHOSH and G. N. MUKHERJEE, *Z. Physik. Chem. (N.F.)*, 1974, **88**, 69 ; *Indian J. Chem.*, 1974, **12**, 636 ; 1975, **13**, 1206 ; *J. Indian Chem. Soc.*, 1975, **52**, 1087 ; 1978, **55**, 813.
6. K. NAKANISHI and P. H. SOLOMON, *Infrared Spectroscopy* (Second Edn.), Holden-Day, Inc., London, 1977, 36-50, 264.
7. A. I. VOGEL, Text Book of Practical Organic Chemistry (ELBS), 1968, p. 177.
8. H. M. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.*, (a) 1954, 2904 ; (b) 1953, 3397.
9. F. J. C. ROSSOTTI and H. S. ROSSOTTI, The Determination of Stability Constants, McGraw Hill, London, 1961, (a) p. 99 ; (b) p. 88.
10. G. N. MUKHERJEE (Unpublished).

J. Indian Chem. Soc.,
Vol. LVII, January 1980, pp. 42-45

*p*H-metric Studies on Quaternary Mixed Ligand Complex Formation of Ni(II)

ABHA MISRA, SHASHI MITAL and G. K. CHATURVEDI

Chemical Laboratories, Agra College, Agra

Manuscript received 19 January 1979, accepted 29 December 1979

Mixed ligand complexes of the type MABC, where M = Ni(II), A = oxalic (OX), malonic (MALN) or phthalic (PHA) acids, B = ethylenediamine (en) or 1,2-diaminopropane (pn) and C = aminoacetic acid (gly) have been investigated by potentiometric titration technique. Evidence is given for the stepwise addition of B and C to the initially formed MA complex, resulting in ternary (MAB) and quaternary (MABC) complex formation respectively. Formation constants (log K_{MABC}) and the free energies of formation (ΔF°) for the quaternary systems have been calculated at 25 ± 1°. The order of stability in terms of diamine have been found to be as pn > en.

THE binary as well as the ternary complexes of transition metals have been extensively investigated. Scanty references are, however, available on quaternary systems such as Fe(III)-NTA-EDTA-phenol[1] and UO_2(II)-A-B-C[2,3] (A, B and C are the different dibasic acids). It has, therefore, been thought worthwhile to investigate quaternary systems involving some other transition metals.

The potentiometric studies of the quaternary system Ni(II)-dicarboxylic acids (H_2A)-diamines (Am)-gly (where H_2A = oxalic(OX), malonic (MALN), phthalic(PHA) acids, Am = ethylenediamine(en), 1,2-diaminopropane(pn), have been carried out. The results of these studies have been discussed in the present communication.

Experimental

Materials :

All the chemicals used were either of BDH (A.R.) or S. Merck (G.R.) grade. The stock solution of $Ni(NO_3)_2 \cdot 6H_2O$ was prepared in double-distilled water and the metal was estimated as $Ni(C_4H_7O_2N_2)_2$[4]. The solutions of ligands oxalic, malonic, phthalic, glycine and dihydrochlorides of ethylenediamine and 1,2-diaminopropane were prepared by dissolving the appropriate weighed amount of the respective materials in double-distilled water. The concentrations of the ligand solutions were further checked by potentiometric titration using 0.1*M* KOH.

Instrument and Methods :

The *p*H-titrations were carried out at 25 ± 1° (maintained thermostatically) with the help of Philips Precision *p*H-meter (PR 9405*M*) standardised against 0.05*M* solution of potassium hydrogen-phthalate.

The total volume of the solution (50 ml), ionic strength ($\mu = 0.1M$ KNO_3) and the concentration in metal and ligands ($5 \times 10^{-3}M$) were kept constant at the beginning of the titration. All the titrations were performed in duplicate to establish the reproducibility of the measurements.

The following sets of solutions were titrated and the *p*H units were plotted against m (m = moles of base added per mole of metal ion or ligands) :

1. 10 ml ($5 \times 10^{-3}M$) $Ni(NO_3)_2$;
2. 10 ml ($5 \times 10^{-3}M$) OX/MALN/PHA/gly ;
3. 10 ml ($5 \times 10^{-3}M$) en.2H⁺/pn.2H⁺ ;
4. 10 ml ($5 \times 10^{-3}M$) $Ni(NO_3)_2$ + 10 ml ($5 \times 10^{-3}M$) OX/MALN/PHA/gly ;
5. 10 ml ($5 \times 10^{-3}M$) $Ni(NO_3)_2$ + 10 ml ($5 \times 10^{-3}M$) en.2H⁺/pn.2H⁺ ;
6. 10 ml ($5 \times 10^{-3}M$) $Ni(NO_3)_2$ + 10 ml ($5 \times 10^{-3}M$)en.2H⁺ + 10 ml (5×10^{-3} *M*) OX/MALN/PHA/gly ;
7. 10 ml ($5 \times 10^{-3}M$) $Ni(NO_3)_2$ + 10 ml ($5 \times 10^{-3}M$) pn.2H⁺ + 10 ml ($5 \times 10^{-3}M$) OX/MALN/PHA/gly ;
8. 10 ml ($5 \times 10^{-3}M$) $Ni(NO_3)_2$ + 10 ml ($5 \times 10^{-3}M$) en. 2H⁺ + 10 ml ($5 \times 10^{-3}M$) OX/MALN/PHA + 10 ml ($5 \times 10^{-3}M$) gly ;
9. 10 ml ($5 \times 10^{-3}M$) $Ni(NO_3)_2$ + 10 ml ($5 \times 10^{-3}M$) pn.2H⁺ + 10 ml ($5 \times 10^{-3}M$) OX/MALN/PHA + 10 ml ($5 \times 10^{-3}M$) gly.

Calculations :

The dissociation constants of the ligands (OX, MALN, PHA, en.2H⁺ and gly) were determined by the method of Chaberek and Martell[5] (Table 1).

TABLE 1—IONISATION CONSTANTS OF THE LIGANDS
$t = 25 \pm 1°C$, $\mu = 0.1M$ KNO_3

Ligand	pK_1	pK_2
Oxalic acid (OX)	1.64±0.19	4.10±0.06
Malonic acid (MALN)	2.78±0.10	5.84±0.09
Phthalic acid (PHA)	3.08±0.09	5.60±0.09
Ethylenediamine (en)	6.96±0.02	10.01±0.07
1,2-diaminopropane (pn)	6.91±0.08*	9.78±0.02*
Glycine (gly)	9.66±0.05	—

* value taken from the literature[6].

The pK values of pn.$2H^+$ have been taken from the literature[6].

The formation constants of the quaternary complexes were calculated by employing the method of Thompson and Loraas[7]. The free energies of formation ($\Delta F°$) were calculated by the following expression :

$$\Delta F° = -RT \ln K_{MABC}$$

where R = gas constant (1.987 K cal/mole/deg,)
T = temperature in absolute degree

and K_{MABC} = overall formation constant of the quaternary complex.

Results and Discussion

The curves a (gly) and b (en. $2H^+$) (Fig. 1) give inflections at m = 1 which in the case of gly is ill-defined.

In the system Ni(II)-en.$2H^+$/OX the inflection at m = 2 (Fig. 1, curve e, g) and at m = 1 in the case of Ni(II)-gly (Fig. 1, curve d) may be attributed to the formation of 1 : 1 binary species. The inflection at m = 3 (Fig 1, curve e, g) in the case of Ni(II)-en. $2H^+$/OX, and at m = 2 (Fig. 1, curve d) in the case of Ni(II)-gly systems at higher pH may be ascribed to the disproportionation of the initially formed 1 : 1 binary complex into 1 : 2 Ni(II)-en.$2H^+$/OX/gly complex.

The curves f, h and i (Fig. 1) represent the 1 : 1 : 1 Ni(II)-en-gly, Ni(II)-OX-gly and Ni(II)-OX-en systems respectively.

Curve i (Fig. 1) for 1 : 1 : 1 Ni(II)-OX-en system overlaps the curve e for 1 : 1 Ni(II)-OX system up to m = 2 in the lower pH-range indicating the preference of OX for metal ion in the initial stages. The two inflections at m = 2 and m = 4 may be attributed to the successive stepwise addition of OX and en.$2H^+$ to the metal ion resulting in the formation of 1 : 1 : 1 Ni(II)-OX-en complex. The non-superimposable nature of the composite curve T' (drawn by adding the horizontal distances of the curves for 1 : 1 Ni(II)-OX system and en.$2H^+$), in the region of ternary complex formation further supports the existence of a mixed ligand ternary species.

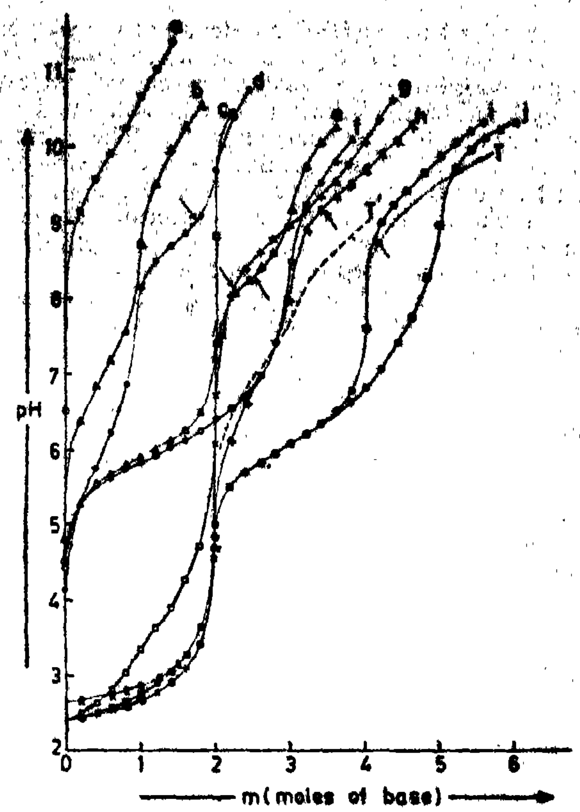
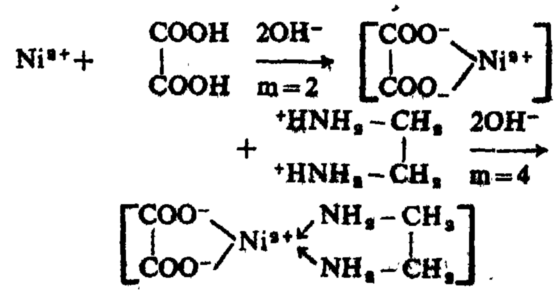


Fig. 1.

Curve a – gly
„ b—en.$2H^+$
„ c—OX
„ d—1 : 1 Ni-gly
„ e—1 : 1 Ni-en.$2H^+$
„ f—1 : 1 : 1 Ni-en.$2H^+$-gly
„ g—1 : 1 Ni-OX
„ h—1 : 1 : 1 Ni-OX-gly
„ i—1 : 1 : 1 Ni-OX-en.$2H^+$
„ j—1 : 1 : 1 : 1 Ni-OX-en.$2H^+$-gly
„ T & T'—Composite curves
→ indicates the appearance of turbidity

The addition of the primary and the secondary ligands to the metal ion resulting in the formation of the biligand species may be expressed as :



Similarly in the case of Ni(II)-OX-gly and Ni(II)-en-gly systems OX and en.$2H^+$ respectively act as primary ligand and glycine as a secondary one.

Curve j (Fig. 1) representing 1 : 1 : 1 : 1 Ni(II)-OX-en-gly system, in the initial stages, superimposes the

curve g for 1 : 1 Ni(II)-OX system up to m=2 and curve i for 1 : 1 : 1 Ni(II)-OX-en up to m=4. This superimposition of the quaternary curve j undoubtedly indicates the behaviour of OX and en.$2H^+$ as primary and the secondary ligands. The addition of the tertiary ligand-glycine to the intermediate 1 : 1 : 1 Ni(II)-OX-en species, however, appears to occur afterwards. Thus the inflections at m=2, m=4 and m=5 in curve j may respectively be attributed to the stepwise addition of OX, (to the metal ion) en.$2H^+$ and gly (to the intermediate 1 : 1 : 1 Ni(II)-OX-en complex) resulting in the formation of a soluble triligand or quaternary 1 : 1 : 1 : 1 Ni(II)-OX-en-gly species. The intermediate step showing the addition of en.$2H^+$ to the binary Ni(II)-OX complex is evidenced by the superimposition of the quaternary curve j with the ternary curve i for Ni(II)-OX-en.$2H^+$ system up to m=4. The inflection at m=4 indicating the step of addition of en.$2H^+$ is, however, not observed in the quaternary curve.

The non-appearance of the precipitate and the non-superimposable nature of the composite curve T (drawn by adding the horizontal distances of the curves for 1 : 1 : 1 Ni(II)-OX-en and gly) further support the formation of the quaternary species.

In Fig. 2, the curves e and g (respectively for 1 : 1 Ni(II)-OX and Ni(II)-pn.$2H^+$), f and i (respectively for 1 : 1 : 1 Ni(II)-pn-gly and Ni(II)-OX-pn) and curve j, (for 1 : 1 : 1 : 1 Ni(II)-OX-pn-gly) being identical in nature to the corresponding systems involving en $2H^+$, may be interpreted in a similar manner.

The quaternary systems involving other dicarboxylic acids (MALN, PHA), diamine (en or pn) and glycine have also been studied but only representative curves for the systems involving oxalic acid and en pn have been given, others being identical are ommitted for the brevity's sake. The formation of triligand species in all these cases has, however, been indicated on the basis of potentiometric titrations and the analysis of the data.

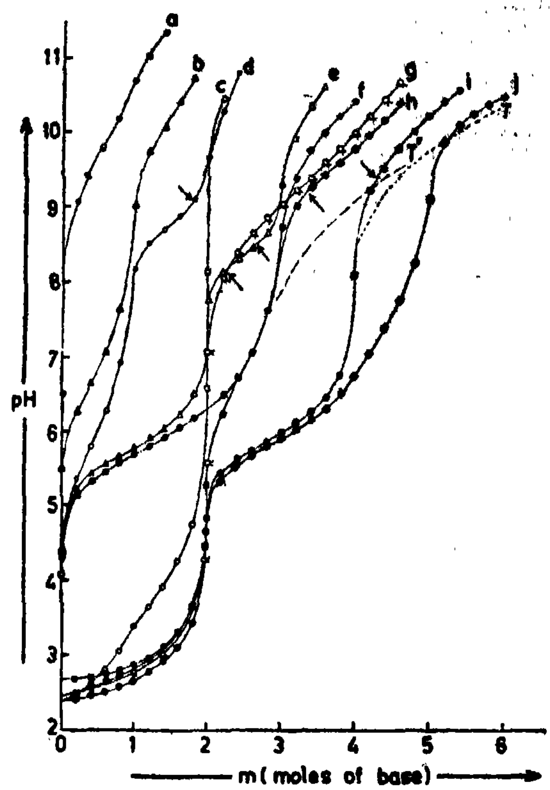


Fig. 2.

Curve a—gly
„ b—pn.$2H^+$
„ c—OX
„ d—1 : 1 Ni-gly
„ e—1 : 1 Ni-pn $2H^+$
„ f—1 : 1 : 1 Ni-pn.$2H^+$-gly
„ g—1 : 1 Ni-OX
„ h—1 : 1 : 1 Ni-OX-gly
„ i—1 : 1 : 1 Ni-OX-pn.$2H^+$
„ j—1 : 1 : 1 : 1 Ni-OX-pn.$2H^+$-gly
„ T & T'—Composite Curves
→indicates the appearance of turbidity

The calculation for the stepwise addition of diamine/gly and the overall formation constants for the quaternary species at 25±1° have been calculated and are recorded in Table 2. The free

TABLE 2—AT 25±1°C

Quaternary systems	log K_{MA}	log K_{MAB}	log K_{MABC}	Overall stability constants	Overall ΔF° K cal/mole
Ni-OX-en-gly	5.3*	7.38±0.06	4.52±0.10	17.20	−23.448
Ni-OX-pn-gly	5.3*	7.48±0.15	4.72±0.20	17.50	−23.852
Ni-MALN-en-gly	4.14*	6.35±0.14	4.08±0.19	14.57	−19.858
Ni-MALN-pn-gly	4.14*	6.45±0.15	4.12±0.12	14.71	−20.049
Ni-PHA-en-gly	3.38±0.18	7.44±0.18	5.43±0.20	16.25	−22.148
Ni-PHA-pn-gly	3.38±0.18	7.72±0.20	5.20±0.18	16.30	−22.216

* values taken from the literature[8].

energies of formation (ΔF°) at $25 \pm 1^{\circ}$ have also been evaluated.

A comparison of the overall formation constants ($\log K_{MABC}$) given in Table 2 indicate the order of stability of the quaternary complexes in terms of secondary ligands as pn>en which follows the order of their basicities.

Acknowledgement

Authors thank Dr. J. P. Tandon, Prof. in Chemistry, Rajasthan University, Jaipur for his valuable suggestions, Agra College authorities for laboratory facilities and Council of Scientific and Industrial Research for awarding a JRF to one of them (A.M.)

References

1. S. Koch and G. Ackermann (Sekt. Chem., Bergakad Freiberg. Freiberg. E. Ger.) *Z. Anorg. Allg. Chem.*, 1976, **420**(1), 95.
2. S. Ramamoorthy and M. Santappa, *J. Inorg. Nuclear Chem.*, 1971, 33(6), 1775.
3. Vinod Kumari and G. K. Chaturvedi, *J. Indian Chem. Soc.*, 1978, **55**, 819.
4. I. Vogel, "Quantitative Inorganic Analysis", Longmans Green & Co. Ltd., 1955, 417.
5. S. Chaberek, Jr. and A. E. Martell, *J. Amer. Chem. Soc.*, 1952, **74**, 5052.
6. G. Sharma and J. P. Tandon, Verlagder *Zeitschrift fur Naturforsch.* Tubingen Band, 1970, **25b**, Heft 1.
7. L. C. Thompson and J. A. Loraas, *Inorg. Chem.*, 1963, **2**, 89.
8. A. E. Martell and Melvin Calvin, "Chemistry of the Metal Chelate Compounds", Prentice-Hall, Inc. Englewood Cliffs. N.J., 1962.

J. Indian Chem. Soc.,
Vol. LVII, January 1980, pp. 46-49

Potentiometric Determination of Protonation Constant of 4,5-Dimethyl-2-Hydroxy Acetophenone and its Oxime‡

(Mrs.) M. MITTAL, KEEMTI LAL and S. P. GUPTA*

Chemical Laboratories, D. N. College, Meerut-250 002

Manuscript received 21 May 1979, accepted 30 November 1979

Protonation constant of 4,5-dimethyl-2-hydroxy acetophenone and its oxime has been determined in aqueous-dioxane [20 to 75% (v/v)] at different ionic strengths (0.01M to 0.1M $NaClO_4$) and temperatures 20°, 30° & 40° potentiometrically. The value of change in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) have been calculated. The value of pK_m^H (minimum pK_1^H value at $\theta°$) has been calculated from Harned's equation.

O-HYDROXY acetophenones and their oximes are very interesting reagents in respect of their complexing property. These ligands have been shown to be useful reagents for spectrophotometric and gravimetric estimations of a numbers of the transition metals[1-4]. However, relatively few studies of their chelating properties have been reported[5-9]. The systematic study of the chelating properties of the disubstituted 2-hydroxy acetophenones and their oximes have been undertaken in this laboratory[9]. In the present communication, the protonation constant of 4,5-dimethyl-2-hydroxy acetophenone (DMHA) and its oxime (DMHAO) have been calculated in aqueous-dioxane medium at different ionic strengths (μ) and temperatures by the method of Irving and Rossotti[10]. Thermodynamic functions and pK_m^H (minimum pK_1^H value at $\theta°$) have been calculated. The effect of the change in dielectric constant, temperature and on pK_1^H value has also been studied.

Experimental

Reagents and Apparatus :

The ligands were prepared as described earlier[11]. Solutions of sodium hydroxide and perchloric acid B.D.H. (AnalaR) were prepared and standardized as usual. Sodium perchlorate (Reidel) was used to maintain the desired ionic strength. Dioxane was purified by the method described by Vogel[12]. An inert atmosphere was maintained by bubbling nitrogen through the solution.

The pH measurements were made with systronic digital pH meter type 335 with a sensitivity of 0.01 unit. The pH meter was calibrated at pH 4.05 and 9.18 with aqueous potassium hydrogen phthalate and borax buffers respectively.

In aqua-dioxane mixtures the pH values were corrected by the use of Van-Uitert and Hass equation[13-16].

$$-\text{Log}\,[H^+] = B + \log U_H$$

where B = pH meter reading and U_H conversion factor. The conversion factor was obtained from the difference between the 'B' and the theoretical value $-\log\,[H^+]$.

The value of log U_H at a fixed temperature can be obtained for any ionic strength from the expression :

$$\text{Log}\,U_H = \log U_H^0 + \log \gamma\pm$$

where $\gamma\pm$ is the activity coefficient and log U_H^0 is the correction at zero ionic strength in the solvent under study.

Procedure :

The experimental procedure of Irving and Rossotti[10] was used for potentiometric titrations of the following thermostated solutions in nitrogen atmosphere :

(i) : 2.0 ml $HClO_4$ (0.05 *M*),
(ii) : (i) +5.0 ml ligand (0.01 *M*)

against standard carbonate free sodium hydroxide (0.05 *M*). The ionic strengths, 0.1 *M*, 0.05 *M* and 0.01 *M* were maintained by the addition of appropriate sodium perchlorate solutions and keeping the total volume at 40.0 ml. Such titrations were carried out in different dioxane-water mixtures.

Calculations :

The Irving and Rossotti's method[10] was used for the calculations of $\bar{n}_H$ (average number of

‡ Paper presented at Annual Convention of Chemist, held at kurukshetra on 23-27 Sept, 1979.

TABLE 1—Log K_1^H VALUES FOR DMHA AND DMHAO IN DIOXANE-WATER SYSTEM AT 30±0.2°C

Ligand	Dioxane-Water% (v/v), μ=0.1M					Dioxane-Water 75% (v/v) Ionic Strength (M)		
	0*	20	40	60	75	0.05	0.01	0.00**
DMHA	9.60	9.98	10.42	11.35	12.18	12.36	12.58	12.70
DMHAO	8.20	8.57	9.05	9.94	10.76	10.87	11.12	11.30

* By Extrapolation to zero percentage Dioxane.
** By Extrapolation to zero Ionic strength.

protons associated with the ligand) from the titration curves. The pK_1^H was obtained from the formation curve between $\bar{n}_H$ and pH, at $\bar{n}_H=0.5$. The value was also calculated using pointwise calculation method and least square method. The values obtained from different methods were in good agreement. The average value of pK_1^H in various percentage (v/v) of dioxane and different ionic strengths are reported in Table 1.

The experimental accuracy of the protonation constant values can be varified by comparing the values of $\bar{n}_H$ found experimentally and those of calculated from the equation :

$$\bar{n}_H=\frac{\Sigma\beta_i[H^+]^i}{1+\Sigma\beta_i[H^+]^i}$$

The difference between $\bar{n}_H$ (exp.) and $\bar{n}_H$ (cal.) is found to be smaller than 10% in most of the cases.

Results and Discussion

The introduction of a methyl group at any position in benzenering results in weakening the acid strength of *o*-hydroxy acetophenone (HA). This is due to the electron releasing nature of the methyl group. The methyl group effect on pK_1^H value of HA due to :

(i) Induction effect of methyl group.

(ii) Increase intramolecular hydrogen bonding between hydrogen of phenolic –OH and oxygen of C=O group[17,18].

(iii) Degree of solvation of ligand in solution.

The pK value of HA(11.85) was obtained in 75% dioxane at 30° and ionic strength 0.1M ($NaClO_4$) by Kamat and Dator[4]. In the present case the value is 12.18, the higher value is due to the substitution of $-CH_3$ groups but above said effects are smaller due to enlarged distance over which it has to operate.

It is interesting to examine the influence of substitution of an oximino group for a keto-oxygen. Comparison of the pK value of corresponding ketone and keto-oxime shows that in all the cases studied the oxime has been found to be a stronger acid than ketone. This may be due to the intramolecular hydrogen bond present in the system as under :

(i) The O–H......N bond that may be expected to be present in the neutral oxime molecule is weaker than the O–H......O bond of the corresponding ketone. Consequently the release of phenolic hydrogen of the oxime is facilitated.

(ii) Another acid strengthening factor is the additional stability of the oxime anion due to the possibility of hydrogen bond formation by oxygen of phenolic group and hydrogen of oximino group.

Therefore, the pK value of DMHAO was found lower i.e. 10.76.

Effect of Varying Dielectric Constant :

With the dissociation of an acid the number of ions in solution increases. The degree of dissociation of acid depends on the dielectric constant (ε) of the medium. A solvent of low dielectric increases the electrostatic force between the ions and facilitate the formation of molecular species resulting in an increase pK value[19] (Table 1). The dielectric constant decreases with increase in dioxane percentage[20].

The change in pK_1^H with mole fraction of dioxane (n_2) is considered for the ligands under study. It gives a linear curve obeying the straight line relationship : $pK_1^H=mn_2+C$, where m and C are slope of the line and intercept (pK_1^H at 0.0% dioxane) respectively. The values of m and C are 7 and 9.6 for DMHA and 9.7 and 8.2 for DMHAO respectively. The pK_1^H do not vary linearly with the reciprocal of ε of the medium at high percentage of dioxane.

Effect of Ionic Strength :

According to Huckel[21] the interaction of the ions decrease with the increase in the μ of the medium in which the reactions are studied. Thus on increasing the μ of the medium, the protonation constant decreases.

TABLE 2—DISSOCIATION CONSTANTS AND THERMODYNAMIC PARAMETERS AT DIFFERENT TEMPERATURES AND ΔH CALCULATED FROM HARNED'S EQUATION FOR DMHA AND DMHAO AT μ=0.10 M($NaClO_4$)

Temp. (°K)	pK_1^H (average)	pK_m^H	$-\Delta G$ (K cal mole^{-1})	$-\Delta H$ (K cal mole^{-1}) (average)	ΔS (Cal deg^{-1} mole^{-1})	$-\Delta H^*$ (K cal mole^{-1})
			DMHA			
293	12.35		16.58		29.27	7.75
303	12.18	10.45	16.91	8.01	29.39	7.87
313	11.97		17.17		29.27	7.95
			DMHAO			
293	10.97		14.73		28.07	7.95
303	10.76	8.89	14.94	7.97	28.01	8.06
313	10.59		15.19		28.07	8.17

* ΔH Using Harned's Equation.

The formation curves ($\bar{n}_H$ vs pH) were drawn at different μ. There was no change in the shape of the curves, suggesting the various species coexist in solution. The pK_1^H value also decrease with increase in the value of μ. Thermodynamic protonation constant were obtained by extrapolation the values of log K_1^H to zero ionic strength from the graph between log K_1^H vs $\mu^{\frac{1}{2}}$.

Effect of Varying Temperature :

The temperature of the titration vessel was changed to the desired temperature and pH of the solution was noted on addition of NaOH.

The ionization constant of a weak acid is a function of temperature and generally it has a maximum value near room temperature. An examination of the data given in Table 2 reveals that pK_1^H value of the ligands decreases as the temperature is raised. The thermodynamic values such as free energy change ($-\Delta G$), enthalpy (ΔH) and entropy (ΔS) for the ionization of ligands in 75% (V/V) dioxane water medium are calculated using the usual expressions :

$$\Delta G = -2.303 \text{ RT} \log K$$

$$\Delta H = 2.303 R \frac{T_2 . T_1}{T_2 - T_1} \log \frac{K''}{K'}$$

$$\Delta S = 2.303 \text{ R} \log K + \frac{\Delta H}{T}$$

where log K″ and log K′ are the protonation constants at the absolute temperature T_2 and T_1 respectively.

The value of pK_m^H (minimum pK_1^H value at $\theta°$) was calculated by Harned's equation :

$$pK_1^H - pK_m^H = C\,(t-\theta)^2$$

where C = constant (5.0×10^{-5} degree^{-2}) on rearrangement:

$$(pK_1^H - Ct^2) = -2C\theta t + (pK_m^H + C\theta^2)$$

Thus the plot of $(pK_1^H - Ct^2)$ vs t should be straight line with a slope of $-2C\theta$ and intercept $(pK_m^H + C\theta^2)$. The value of $pK_1^H - Ct^2$ for the ligands were plotted against temperature and it was observed that the plot is linear from this plot, the value of θ and pK_m^H were obtained and reported in Table 2. The plot pK_1^H Vs temperature is also linear. It has been observed by Harries and Wright[24] that this temperature range is so far removed from the plot of pK_1^H vs temperature and is the linear portion of the parabola[24].

The value of ΔH was also calculated by Harned's[28] equation :

$$\Delta H = 2.303 \text{ RT}^2 \,(t-\theta) \times 10^{-4}$$

and are reported in Table 2.

Acknowledgement

One of us (MM) thanks to U.G.C. (New Delhi) for awarding teacher's fellowship.

References

1. S. N. PODDAR, *Z. analyt. Chem.*, 1957, **154**, 254 ; 1957, **155**, 327.
2. H. SINGH and K. C. SHARMA, *Indian J. Appl. Chem.*, 1965, **28**, 48.
3. M. H. GANDHI and M. N. DESAI, *Analyt. Chem. Acta*, 1968, **43**, 388.
4. K. LAL and S. P. GUPTA, *Indian J. Chem.*, 1975, **13**, 979 ; *Curr. Sci.*, 1975, **44**, 178.
5. L. B. MAGNUSSON, C. POSTMUS JR. and C. A. CRAIG., *J. Amer. Chem. Soc.*, 1963, **85**, 1711.
6. P. V. KAMAT and M. G. DATOR, *J. Indian Chem. Soc.*, 1970, **47**, 409 ; 1972, **49**, 261.
7. C. B. PATEL and R. P. PATEL, *J. Indian Chem. Soc.*, 1975, **52**, 812.
8. V. SESHAGIRI and S. BRAHMAJI RAO, *J. Inorg. Nuclear Chem.*, 1974, **36**, 353.
9. K. LAL, Ph.D. Thesis, Meerut University, Meerut, 1976.

. H. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.*, 1953, 3397 ; 1954, 2904.

1. (Mrs). M. MITTAL, K. LAL and S. P. GUPTA, *Metals & Min. Review*, 1978 (accepted).

A. I. VOGEL, "A Text Book of Practical Organic Chemistry", Longmans Green & Co., London, 1956, 177.

3. L. G. VAN UITERT and C. G. HASS, *J. Amer. Chem. Soc.*, 1953, **75**, 451.

1. I. D. CHAWLA and C. R. SPILLERT, *J. Inorg. Nuclear Chem.*, 1968, **30**, 2717.

5. B. RAO and H. B. MATHUR, *J. Inorg. Nuclear Chem.*, 1971, **33**, 3919.

3. K. LAL, *Indian J. Chem.*, 1979, **17A**, 314 ; *Talanta*, 1979, **26**, 1171.

7. R. P. PATEL and R. D. PATEL, *J. Inorg. Nuclear Chem.*, 1970, **32**, 2591.

18. L. N. FERGUSON, "The Modern Structural Theory of Organic Chemistry", Printice Hall, New Delhi, 1969.

19. M. GIULIO, "Electro Chemistry, Principles, Practices and Applications", Elsevier Amsterdam, 1963, 80.

20. A. J. GERMANY, *J. Chem. Phys.*, 1942, **10**, 723.

21. H. S. HARNED and B. B. OWEN, "The Physical Chemistry of Electrolytic Solutions", Reinhold, New York, 1958, 113.

22. E. HUCKEL, *Physik Z.*, 1925, **26**, 93.

23. H. S. HARNED and L. KAZANJIAN, *J. Amer. Chem. Soc.*, 1936, **58**, 1912.

24. H. J. HARRIES and G. WRIGHT, *J. Inorg. Nuclear Chem.* 1969, **31**, 3149.

J. Indian Chem. Soc.,
Vol. LVII, January 1980, pp. 50-52

Gravimetric Determination of Nickel(II) and Palladium(II) and Their Separation from Binary Mixture with 3-(p-Acetophenyl)-1-Methyltriazene-N-oxide

B. C. RAY, N. R. BISWAS and S. LAHIRI*

Department of Chemistry, Jadavpur University, Calcutta-700 032

Manuscript received 14 September 1979, accepted 30 November 1979

3-(p-Acetophenyl)-1-methyltriazene-N-oxide has been used successfully for gravimetric determination of Nickel(II) (3-30 mg) and Palladium(II) (2.5-40 mg) with an accuracy of ±0.14% and ±0.16% respectively. The precipitation of Ni and Pd complexes start at pH 5.0 and 0.5 and are quantitative within the pH range 6.5-10.2 and 1.0-8.0 respectively. The greenish yellow coloured Ni-complex and buff coloured Pd-complexes correspond with the formula $Ni(C_9H_{10}O_2N_3)_2.2H_2O$ and $Pd(C_9H_{10}O_2N_3)_2$ respectively and can be weighed as such after drying at 120°. The reagent has also been used in the separation and determination of one in its binary mixture with the other. Determinations in presence of different foreign ions have also been reported.

DIMETHYL glyoxime[1] is the most widely applied and accepted gravimetric reagent for both Ni(II) and Pd(II). Objections to the precipitation of Pd(II) with DMG are the voluminous character of the precipitate and interference due to Platinum and Nickel. The other reagents comprising of various thioligands[2-4], triazenes[5-7] have also been reported for the determination of either the Ni(II) or Pd(II) or both, but most of them involve narrow *p*H-range and/or consume much time. In this paper we recommend the reagent, 3-(*p*-acetophenyl) 1-methyltriazene-N-oxide[8] which reacts with Nickel(II) and Palladium(II) quantitatively in the *p*H range 6.5-10.2 and 1.0-8.0 forming thermally stable greenish yellow $Ni(C_9H_{10}O_2N_3)_2.2H_2O$ and buff coloured $Pd(C_9H_{10}O_2N_3)_2$ complexes respectively. The estimation procedures recommended for both the metal ions Ni(II) and Pd(II) are very simple, cover wide *p*H-range and consume much less time. The compact nature of the precipitates render them easily washable with redistilled water only. As there lies a clear margin in the *p*H ranges for the estimation of the two metal ions they can be separated from their binary mixtures simply by controlling the *p*H. The interferences due to almost all ions have been removed by controlling *p*H or using suitable masking agents.

Experimental

3-(p-Acetophenyl)-1-methyltriazene-N-oxide : The reagent was prepared by the method as reported[8].

Nickel(II) solution : Nickel chloride (E. Merck) was dissolved in very dilute hydrochloric acid and the metal content was determined gravimetrically with dimethylglyoxime[1].

Palladium(II) solution : Palladium chloride (E. Merck) was dissolved in strong hydrochloric acid and palladium was estimated also with dimethylglyoxime[1].

Diverse ions : Solutions of other ions were prepared from the chloride or nitrate salts of cations and from the sodium, potassium and ammonium salts of anions. A few drops of suitable acid was added to prevent hydrolysis where necessary. All the chemicals used were of analytical grade.

Apparatus : All the *p*H measurements were carried out with a cambridge bench model *p*H-meter.

Determination of Nickel(II) : To an aliquot of standard solution of nickel (3.0-30.0 mg) present in 200 ml at *p*H 3.0-4.0 heated on a boiling water bath, solution of the reagent (30.0-250.0 mg) in ethanol was added with stirring. The *p*H then raised gradually with ammonia solution to 6.5-10.2. The greenish yellow precipitate was digested for half an hour. The complex was then filtered through weighed gooch crucible (No. 4) and washed with hot (80°) water and dried at 120° and weighed as $Ni(C_9H_{10}O_2N_3)_2.2H_2O$ to constant weight. The conversion factor is 0.1226. Results of one of several determinations are furnished in Table 1.

Determination of Palladium(II) : The procedure is almost the same as that of nickel. To the palladium solution (2.5-40 mg) present in 200 ml heated on a boiling water bath, the reagent (20.0-240.0 mg) dissolved in minimum volume of alcohol was added gradually with stirring. The *p*H was

TABLE 1—DETERMINATION OF NICKEL AND PALLADIUM

Metal ion taken	Weight (mg)	Wt of the complex (mg)	Metal ion found (mg)	Relative error (%)
	3.0	24.5, 24.4	3.00, 2.99	nil, −0.33
	12.0	97.8, 98.0	11.99, 12.01	−0.08, +0.08
Ni^{2+}	21.0	171.3, 171.0	21.00, 20.96	nil, −0.19
	30.0	244.7, 245.0	30.00, 30.03	nil, +0.10
	2.48	11.41, 11.45	2.47, 2.48	−0.40, nil
	9.92	45.71, 45.66	9.91, 9.90	−0.10, −0.20
Pd^{2+}	19.84	91.60, 91.42	19.86, 19.82	+0.10, −0.10
	39.68	183.08, 183.30	39.69, 39.74	+0.02, +0.15

then adjusted between 1.0 and 8.0 with ammonia solution. The buff coloured precipitate was kept over the boiling waterbath for digestion till the precipitate quagulated which required 20 minutes. The precipitate then filtered through weighed gooch crucible (No. 3) and washed several times with hot water, dried at 120° and finally weighed as $Pd(C_9H_{10}O_2N_3)_2$. The gravimetric factor is 0.2168. The results ot these determinations are given in Table 1.

Separation and Determination of Ni(II) and Pd(II) Present in a Binary mixture : The *p*H of the binary mixture containing Ni(II) and Pd(II) in solution was adjusted at 2.0 and heated on boiling water bath. Slight excess amount of reagent than what is required for the estimation of the total metal ions, dissolved in alcohol was gradually added with stirring. The precipitate of Pd-complex formed almost instantaneously quagulated on digestion for 20 minutes. It was filtered, washed and the metal content determined as described earlier. The volume of the filtrate containing nickel and the washings was then reduced to 200 ml and the metal content was determined following the procedure described. The results follow in Table 2.

TABLE 2—SEPARATION AND DETERMINATION OF PALLADIUM AND NICKEL FROM BINARY MIXTURES

Metal taken (mg)		Metal found (mg)		Relative error%	
Ni	Pd	Ni	Pd	Ni	Pd
4.50	4.96	4.49	4.97	−0.22	+0.20
4.50	14.88	4.48	14.87	−0.44	−0.07
13.50	4.96	13.48	4.96	−0.15	nil
21.00	21.08	21.05	21.05	+0.23	−0.14

Procedure in Presence of Diverse Ions : When the estimations are to be done in presence of foreign ions, tartrate is added prior to the addition of the reagent and the *p*H-values for Palladium and Nickel estimations are kept at 2.0 and 7.0 respectively. Results of one of the several determinations are recorded in Table 3. Suitable masking agents used in the determinations of Ni and Pd are tartrate in general, phosphoric acid (a), ascorbic acid (b), ammonium acetate (c) and potassium iodide (d) preferably when required. Chromium(III), Manganese(II), Copper(II) and Cobalt(II) do not interfere with the determination of palladium but do with nickel estimation. Disodium EDTA, anions as cyanide and large excess of citrate, oxalate and phosphate also interfere, 100 mg of oxalate, citrate, 200 mg of phosphate are however tolerable in both the cases. Even trace amount of Au(III) interferes with Pd(II) estimation. For determination of either metal ions in presence of Ag(I) and Pb(II) nitric acid was used in place of hydrochloric acid.

TABLE 3—SEPARATION OF NICKEL(II) OR PALLADIUM(II) FROM DIVERSE IONS

Diverse ions (mg)	Ni taken : 9.0 mg		Pd taken : 9.92 mg	
	Ni found (mg)	Relative error%	Pd found (mg)	Relative error%
Tartrate (100)	9.01	+0.11	9.92	nil
Fluoride (500)	9.00	nil	9.90	−0.20
Thiocyanate (100)	8.98	−0.22	interferes	
Arsenate (100)	9.00	nil	9.91	−0.10
Borate (100)	8.99	−0.11	9.89	−0.30
Fe^{3+} (30)	8.97 a,b	−0.33	9.94(a),b	+0.20
Al^{3+} (30)	9.02	+0.22	9.90	−0.20
Bi^{3+} (30)	9.00	nil	9.91	−0.10
As^{3+} (30)	8.99	−0.11	9.89	−0.30
Be^{2+} (50)	9.02	+0.22	9.92	nil
Ni^{2+} (50)			9.90	−0.20
Zn^{2+} (50)	9.00	nil	9.88	−0.40
Hg^{2+} (50)	8.99 (d)	−0.11	9.89	−0.30
Cd^{2+} (50)	9.02 (d)	+0.22	9.92	nil
Pb^{2+} (30)	9.03	+0.33	9.96	+0.30
Ag^{1+} (30)	9.01	+0.11	9.93	+0.10
Mg^{2+} (50)	9.00	nil	9.92	nil
Sn^{2+} (30)	9.02	+0.22	9.88	−0.40
MoO_4^{2-} (50)	8.99	−0.11	9.90	−0.20
WO_4^{2-} (50)	9.00	nil	9.91	−0.10
UO_2^{2+} (50)	8.99c	−0.11	9.88	−0.40
ZrO^{2+} (50)	9.02	+0.22	9.92	nil
HfO^{2+} (50)	8.98	−0.22	9.93	+0.10
VO_3^- (50)	9.01	+0.11	9.91	−0.10
Nb^{5+} (50)	8.99	−0.11	9.89	−0.30
Ta^{5+} (50)	9.02	+0.22	9.92	nil
Rh^{3+} (50)	8.97	−0.33	9.88	−0.40
Pt^{4+} (50)	9.00	nil	9.92	nil
Os^{4+} (50)	9.03	+0.33	9.91	−0.10
TiO^{2+} (50)	9.01	+0.11	9.89	−0.30

Results and Discussion

Effect of pH and Reagent Concentration : With fixed amount of metal content (Ni = 9.0 mg, Pd = 9.92 mg) both nickel and palladium were estimated as described at varying *p*H values. It was found that the precipitation of nickel and palladium complexes start at *p*H 5.0 and 0.5 and are quantitative within the *p*H-range 6.5-10.2 and 1.0-8.0 respectively. At fixed *p*H values (7.0 for nickel and 2.0 for palladium) definite amount of the metal contents were estimated with varying quantities of the reagent. Amount of reagents required for complete precipitation of both the metal ions from its solution was 1.2 times of the theoretical amount of the reagent. Determinations in presence of foreign ions require slight more (2-2.5 times) reagent.

Properties and Composition of the Complexes : Both the nickel and palladium-3-(*p*-acetophenyl)-1-methyltriazene-N-oxide complexes are practically insoluble in water and 30% (v/v) ethanol. The

nickel complex is appreciably soluble in absolute alcohol, acetone, benzene and chloroform, however, the palladium complex is much less soluble in those solvents. Both the complexes are almost insoluble in carbon tetrachloride and ether. The recrystallised greenish-yellow nickel and buff-coloured palladium complexes melt with decomposition at 236° and 265° respectively. Both the complexes were analysed for nitrogen by Duma's method and metal content after decomposing with acid by the usual procedure with DMG. The results obtained were in fair agreement with the theoretical results corresponding to molecular formula

$Ni(C_9H_{10}O_2N_3)_2.2H_2O$ and $Pd(C_8H_{10}O_2N_3)_2$.

[Ni calc : 12.26% N calc : 17.53%]
[Ni Found : 12.16% N found : 17.80%]

[Pd calc : 21.68% N calc : 17.11%]
[Pd found : 21.61% N found : 16.92%]

As the triazene complexes are usually explosive in nature weight loss due to water molecule of the nickel complex could not be tried thermogravimetrically. I.R. spectral bands at 3175 cm^{-1} and 988 cm^{-1} in the free ligand due to N–H and N–O stretches disappears and shifts to lower frequencies respectively in the Ni(II) and Pd(II) chelates. This indicates that chelation takes place through N–H by proton displacement and through 'O' of N–O with the formation of M–O bond. Moreover appearance of a new band at 3150 cm^{-1} in Ni(II) chelate shows the presence of water molecules in the compound. The nickel chelate has been found to be diamagnetic suggesting square planer configuration and hence water molecules present are probably lattice water. Pd(II) complex is as usual diamagnetic and appears to possess square planer stereochemistry.

Precision and Accuracy : The average error for twenty-five determinations for each of the metal ion nickel(II) and palladium(II) are ±0.14% and ±0.16% respectively.

Acknowledgement

The authors are grateful to U.G.C., New Delhi for a Teacher Fellowship awarded to N.R.B. under Faculty Improvement Programme.

References

1. A. I. VOGEL, 'A Text Book of Quantitative Inorganic Analysis, 3rd Ed., Longmans, Green and Co. Ltd., London, 1961, p. 511, 526.
2. S. K. MUKHERJEE and N. C. SOGANI, *Indian J. Chem.* 1977, **15A**, 366.
3. P. K. HALDER, M. MAZUMDER and S. C. SHOME, *J. Indian Chem. Soc.*, 1978, **55**, 784.
4. N. K. DUTTA, and B. K. BHATTACHARJEE, *Indian J. Appl. Chem.*, 1964, **27**, 815.
5. S. C. BHATTACHARYA and N. C. SOGANI, *Analyt. Chem.*, 1956, **28**, 81, 1616.
6. P. D. CHATLANGYA, C. S. BHANDARI and N. C. SOGANI, *J. Indian Chem. Soc.*, 1977, **54**, 1001.
7. S. C. SAHA, D. CHAKRABORTI and P. K. CHAKRABORTI, *Indian J. Chem.*, 1977, **15A**, 816.
8. N. R. BISWAS, B. C. RAY and S. LAHIRI, *J. Indian Chem. Soc.*, 1979, **56**, 473.

J. Indian Chem. Soc.,
Vol. LVII, January 1980, pp. 53-55

Determination of 4-S-Benzyl-1-Parachlorophenyl-5-Phenyl-2, 4-isodithiobiuret in Acetone

D. S. SABDE, B. M. SARIN and R. B KHARAT*

Department of Chemistry, Nagpur University, Nagpur

Manuscript received 3 August 1979, accepted 30 November 1979

Determination of 4-S-Benzyl-1-Parachlorophenyl-5-phenyl-2,4-isodithiobiuret (BPPTB) in acetone medium has been carried out by enthalpimetric, conductometric and potentiometric titrations, using tetra-n-butyl ammonium hydroxide, potassium tertiary butoxide and alcoholic potassium hydroxide as titrants. Concentration range for determination of BPPTB was found to be 0.5 to 8.0 mg for enthalpimetric, 0.5 to 7.0 mg for conductometric and 0.5 to 8.0 mg for potentiometric titrations. Potentiometric titrations gave the best results while enthalpimetric titrations are recommended for simplicity and quickness.

4-S-BENZYL-1-Parachlorophenyl-5-Phenyl-2,4-isodithiobiuret (BPPTB) has been recently used in this laboratory for the solvent extraction studies of transition metals[1], thin layer chromatography of metal chelates[2] and in the structural studies of metal chelates[3]. Looking into its analytical importance, it was thought worthwhile to develope a suitable method for determination of BPPTB in micro-quantities. In the present paper different methods like enthalpimetric titration, conductometric titration and potentiometric titration, have been used to determine the optimum conditions for quantitative estimation of BPPTB.

Experimental

All chemicals used were A.R. Grade. BPPTB was synthesised and recrystalised by the known method[4]. Acetone was purified and made anhydrous[5] by keeping it over $KMnO_4$ for 2 days and then over fused calcium chloride for 2 days. It was then distilled at 56°. Tetra-*n*-butyl-ammonium hydroxide ($TBuNH_4OH$), Potassium tertiary butoxide (tert. BuOK) and alcoholic potassium hydroxide (Alc.KOH) were prepared and preserved as reported previously[6].

Instruments and Apparatus :

Direct reading conductometer with C. C. –01 Elico type conductivity cell (cell constant 0.481) was used for conductometric titration. The cell was conditioned by keeping it in anhydrous acetone for 24 hours before titration.

Direct reading potentiometer was used for potentiometric titrations. Calomel electrode, prepared with $Hg/HgCl_2$ satd. KCl in methyl alcohol was used as referance electrode and pure aluminium wire (99.99%) of 1 mm diameter was used as an indicator electrode. Small portion of aluminium wire (about 2 mm) was cut off by sharp edge just before each titration.

Procedure :

All titrations were carried in nitrogen atmosphere. Methods for enthalpimetric, conductometric and potentiometric titrations were necessarily the same as reported in our previous communication[6]. End points were always determined graphically.

Results and Discussion

(1) *Choice of Proper Titrant :*

Titration curves for enthalpimetric titration of BPPTB by $TBuNH_4OH$ (curve I), tert. BuOK (Curve II) and Alc. KOH (Curve III) are shown in Fig. 1. The end points are indicated by sudden break in the curve accompanied by sharp rise in temperature. Titration curves for conductometric titrations (Fig. 2) did not show sharp break, but the end points could be determined by extrapolation. However errors in estimation were comparatively large.

Potentiometric titration curves (Fig. 3) show sharp rise in potential at the end point. The end points were determined by differential method to get accurate results.

Comparison of the results obtained by three different methods for $TBuNH_4OH$, tert. BuOK and Alc. KOH (Table 1) show that Alc. KOH is the most suitable titrant for estimation of BPPTB.

* For correspondence.

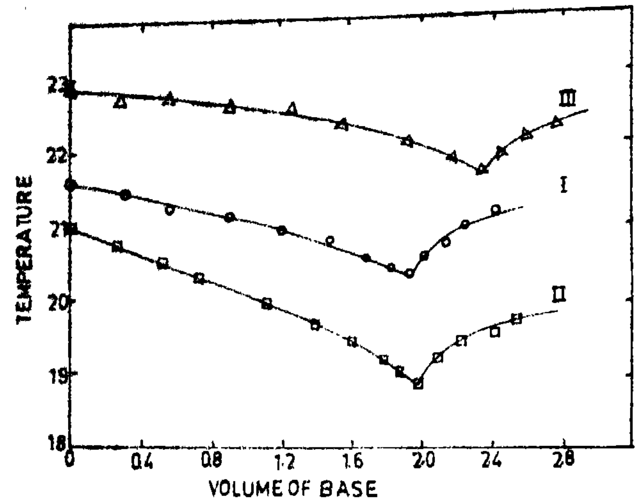


Fig. 1. Enthalpimetric Titrations of BPPTB
I—TBuNH$_4$OH
II—tert. BuOK
III—Alc. KOH

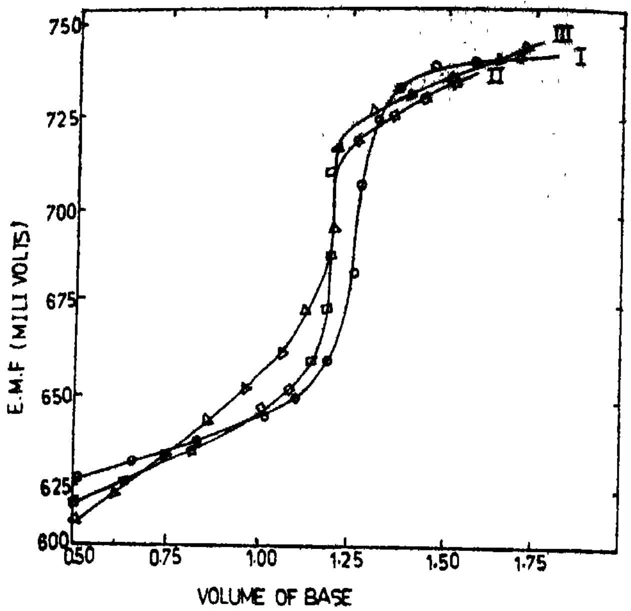


Fig. 3. Potentiometric Titrations of BPPTB
I—TBuNH$_4$OH
II—tert. BuOK
III—Alc. KOH

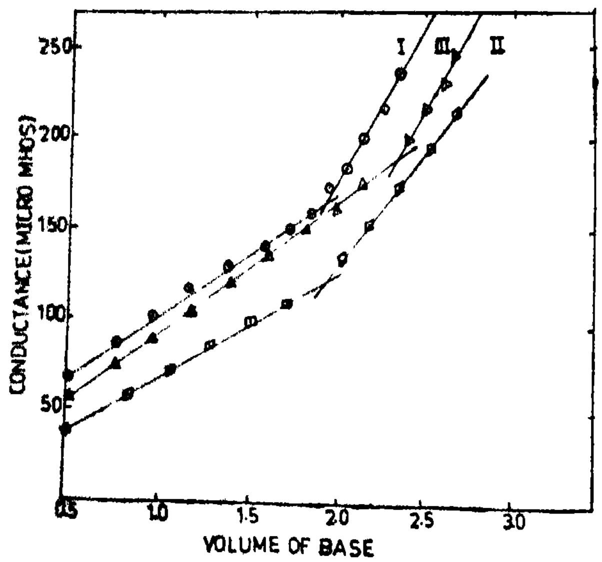


Fig. 2. Conductometric Titrations of BPPTB
I—TBuNH$_4$OH
II—tert. BuOK
III—Alc. KOH

Hence Alc. KOH was used as a titrant for further experiments.

TABLE 2—ENTHALPIMETRIC TITRATIONS OF 4-S-BENZYL-1-PARACHLOROPHENYL-2,4-ISODITHIOBIURET (BPPTB)

Effect of dilution

Solvent-Acetone — Titrant-Alc. KOH

No.	Vol. of soln taken	Vol. of acetone added	Wt. of BPPTB titrated	Wt. found	%error
	ml	ml	mg	mg	
1.	5.0	0.0	2.994	3.011	+0.6
2.	5.0	1.0	2.994	3.011	+0.6
3.	5.0	2.0	2.994	2.968	−0.9
4.	5.0	3.0	2.994	2.982	−0.4
5.	5.0	4.0	2.994	3.011	+0.6
6.	5.0	5.0	2.994	2.968	−0.9
7.	5.0	6.0	2.994	2.968	−0.9

TABLE 1—TITRATIONS OF 4-S-BENZYL-1-PARACHLOROPHENYL-5-PHENYL-2,4-ISODITHIOBIURET (BPPTB)

Effect of nature of titrant

Solvent-Acetone

No.	Titrant	Enthalpimetric Titration			Conductometric titration			Potentiometric Titration		
		Wt. of BPPTB taken	Wt. found	%error	Wt. of BPPTB taken	Wt. found	%error	Wt. of BPPTB taken	Wt. found	%error
		mg	mg		mg	mg		mg	mg	
1.	TBuNH$_4$OH	5.000	4.583	−9.3	4.998	4.017	−19.6	5.040	4.970	−1.4
2.	tert. BuOK	[illegible]	4.637	−7.3	4.998	4.017	−19.6	5.040	4.910	−2.6
3.	Alc. KOH	5.000	4.983	−0.3	4.998	4.820	−3.6	5.040	5.008	−0.6

TABLE 3—TITRATIONS OF 4-S-BENZYL-1-PARACHLOROPHENYL-2,4-ISODITHIOBIURET (BPPTB)

Effect of Concentration of solute

Solvent-Acetone | Titrant-Alc. KOH

No.	Vol. of soln taken ml	Vol. of acetone added ml	Wt. of BPPTB titrated mg	Enthalpimetric titrations Wt. found mg	Enthalpimetric titrations %error	Conductometric titrations Wt. found mg	Conductometric titrations %error	Potentiometric titrations Wt. found mg	Potentiometric titrations %error
1.	0.5	49.5	0.2495	0.043	—	0.0868	—	0.0971	—
2.	1.0	49.0	0.499	0.4962	−0.6	0.5091	+1.8	0.4965	−0.5
3.	2.0	48.0	0.998	1.010	+1.2	0.9814	−1.7	0.9930	−0.5
4.	4.0	46.0	1.996	1.978	−0.9	1.986	−0.5	1.982	−0.7
5.	6.0	44.0	2.994	3.011	+0.6	2.968	−0.9	2.979	−0.5
6.	8.0	42.0	3.992	4.000	+0.2	3.998	0.0	3.989	−0.1
7.	10.0	40.0	4.990	4.947	−0.9	4.901	−0.9	4.952	−0.8
8.	12.0	38.0	5.988	5.907	−1.3	5.882	−1.9	5.972	−0.3
9.	14.0	36.0	6.986	6.923	−0.9	6.865	−1.7	6.943	−0.6
10.	16.0	34.0	7.984	7.843	−1.8	7.728	−3.2	7.917	−0.8
11.	18.0	32.0	8.982	8.604	−4.2	8.592	−4.3	8.713	−3.0
12.	20.0	30.0	9.980	9.450	−5.3	9.520	−4.6	9.585	−4.0

(2) *Effect of dilution :*

Effect of dilution was studied by choosing a particular wt. (3 mg) of BPPTB and enthalpimetric titrations were performed using different volumes of acetone under identical conditions (Table 2). From the results it seems that volume of solvent does not have any noticable effect.

(3) *Effect of concentration of the solute :*

Stock solution containing 4.99 mg of BPPTB per ml was prepared and different volumes of this solution (0.5 to 20.0 ml) were diluted to 50 ml to get the solutions of different concentrations. 5 ml of each of these solutions were separately titrated enthalpimetrically, conductometrically and potentiometrically and the results (Table 3) were compared.

It is observed from Table 3 that BPPTB can be quantitatively estimated between 0.5 mg to 8.0 mg by enthalpimetric titrations. Beyond these limits the percentage error becomes appreciable. Conductometric titrations also gave good results for 0.5 to 7.0 mg of BPPTB, but the percentage errors were relatively large.

Potentiometric titrations were found to yield best results amongst the three methods. Errors in estimation were found to be minimum (usually less than 1.0%) and the method can estimate 0.5 to 8.0 mg BPPTB accurately under the experimental conditions. However, enthalpimetric method surpases the potentiometric method in simplicity and fastness and hence is recommended for quick estimation of BPPTB.

Standard and mean deviations :

Standard and mean deviations for titrations of BPPTB with Alc. KOH were found to be 0.45 and 0.06 for enthalpimetric titrations, 0.04 and 0.81 for conductometric titrations, and 0.03 and 0.31 for potentiometric titrations.

Acknowledgement

The authors are thankful to Dr. K. N. Munshi, Professor and Head of Department for the research facilities.

References

1. B. K. DESHMUKH and R. B. KHARAT, Ph.D. thesis, Nagpur University, Nagpur, 1978.
2. N. S. BHAVE, S. R. DUDHEY and R. B. KHARAT, *Separation Science and Technology*, 1978, 13(2), 193.
3. N. S. BHAVE and R. B. KHARAT, Communicated.
4. A. S. MAHAJAN and M. G. PARANJAPE, *J. Indian Chem. Soc.*, 1974, 51, 287.
5. J. KUCHARSKEY and L. SAFARIK, 'Titrations in Nonaqueous Solvents', 2nd edition, Elsevier Publishing Co, New York, 1974, 49.
6. D. S. SABDE and R. B. KHARAT, *J. Indian Chem. Soc.*, Communicated.

J. Indian Chem. Soc.,
Vol. LVII, January 1980, pp. 56-59

Microdetermination of Metals in Organometallic Compounds by the Oxine Method, Closed Flask or Open Tube Decomposition*

SALAH A. ABOU TALEB

Department of Chemistry, Science & Maths. Center, Riyadh, Kingdom of Saudi Arabia

Manuscript received 16 July 1979, accepted 30 November 1979

Drops of nitric–perchloric acid and hydrogen peroxide digestion mixture, placed in a test tube, have utilized for decomposition of organometallic compounds containing Al, Fe, Cu, U, Co, Ti, Ni, La, Th or Mo. The open tube method, besides being efficient, is convenient and rapid, decomposition occurs within 5-10 minutes. The metal content is estimated using 8-hydroxyquinoline followed by a gravimetric or a titrimetric determination. For every sample weight three results are obtained using three different methods, the average per cent error for the determination is ±0.15, ±0.11 and ± 0.14, respectively. The oxygen flask combustion procedure was extended to Mo, La and Th and the average per cent error for the determination is ±0.23, ±0.14 and ±0.18, respectively.

IN the analysis of organometallic compounds, the method of decomposition together with the method of estimation of the metal content are the two problems involved. The mutual relationship which exists between the method of decomposition and the method of determination to follow is to be taken into consideration.

Decomposition by incineration to sulphate, oxide or the metal itself is not always so reliable[1], after decomposition, gravimetric estimation of the metal content has to go through the problem of selecting the suitable weighing form. Besides the probable danger of loss of substance by sublimation, also few number of metals yield forms stable enough to be recommended for a gravimetric finish. Wet decomposition in sealed tube, using different digestion mixture, has been widely applied some years ago. However, the Carius decomposition, being a time consuming-task, lost much of its popularity. Kjeldahl digestion resembles the Carius decomposition in that both are efficient for mineralising metals from their difficulty decomposable compounds. The relatively high concentration of sulphuric acid restricts, to some extent, the applicability of the technique, neutralization of the acid may cause co-precipitation as a result of the high salt concentration produced. Fusion in the nickel bomb is a rapid means for decomposition, but suffers from the danger of co-precipitation due to the same above reason.

The closed-flask method of combustion[2] has been applied for the analysis of organometallic compounds. The microdetermination of Cd, Mg, U, Zn, Co, Mn, Ti, Cu, Pb, Al, Fe, Ni, Ca and Bi in organometallic compounds using 8-hydroxyquinoline (Oxine)[3] following combustion by the O-Filled Flask method have been described[3-5]; gravimetric and titrimetric procedures were used for the estimation of the metal content. To ensure quantitative combustion, mixing the sample with a Flux sometimes proved a necessity[4,5]. The use of fairly concentrated (1 : 1) acid as absorbent, followed by boiling of the absorption solution was found necessary for combustion of compounds containing iron, alluminium, nickel or bismuth[5]. Moreover, a platinum gauze sample holder is usually satisfactory but a Pyrex glass or silica spiral is used with organobismuth[5] compounds to avoid alloy formation with the platinum holder. This diversity together with the drastic conditions of absorption solution inhabit the merit of the O-filled flask method as a simple and general tool for decomposition of organometallic compounds.

Tauchitani, Tomita and Ueno[6] reported a rapid, convenient and efficient method for decomposing a wide variety of metal chelates; the sample being placed in an open tube charged with a digestion solution of concentrated nitric acid alone or mixed with sulphuric or perchloric acid. Although the method seems promising, a further attempts have been reported to test the capability of the technique for mineralising metals from their organometallic compounds.

In the present work, the open tube method proved satisfactory for decomposition of Al-, Co-, Ti-, U-, Cu-, Fe-, Ni-, La-, Th- or Mo-containing organic compounds. A procedure for combustion of organic compounds containing La, Mo and Th using the closed-flask method is also described. It seems that there is no other method for the determination of any of the three metals in organic

* Submitted in honour of the 50th birthday of Professor Dr. A. B. Sakla

compounds other than the old method of incineration to their oxide, also it seems it is the first time that the oxygen flask combustion procedure was applied for the decomposition of these metals.

Experimental

Reagents and Materials :

All reagents employed are of A.R. grade except where otherwise mentioned. Acetic acid, 10% solution.

Ammonium acetate, 10% solution.

Ammonium hydroxide, concentrated and 10% solution.

Digestion mixture, prepared by mixing three parts of M. A. R. concentrated nitric acid (sp. gr. 1.42) with one part of perchloric acid (sp. gr. 1.70).

Nitric acid, 2*N* solution.

Sodium carbonate, solid.

Hydrochloric acid, M. A. R. concentrated.

Hydrogen peroxide, 100 volume solution.

8-Hydroxyquinoline, 1% solution either in 95% ethanol or in *N*-acetic acid solution.

Potassium bromate, 0.05*N* standard solution, prepared from the M. A. R. grade reagent.

Potassium bromide, 10% solution

Potassium iodide, 10% solution

Sodium thiosulphate, 0.02 *N* solution, prepared from the M. A. R. grade reagent and standardized against the primary standard potassium bromate solution.

Starch, 1% solution.

Sulphuric acid, M. A. R. concentrated

Procedures :

A. Decomposition of organometallic compounds :

(1) Open tube decomposition :

Place an exactly weighed amount (3-6 mg) of the organic sample in a small tube (150 mm long and 15-mm in diameter). Down the walls of the tube, slowly, introduce 10 drops of the digestion mixture followed by 5 drops of hydrogen peroxide. Hold the tube at an angle of 45° and start heating the lower part of the tube using a microburner. Shake the tube regularly to avoid splashing. Continue heating for 5-10 minutes or till nearly dry. Repeat the digestion once more to ensure complete decomposition. Allow to cool down for a few minutes then add 5 ml of water (in case of molybdenum, also introduce 1-2 drops of concentrated ammonia and shake to dissolve the residue).

(2) Closed flask combustion of organometallic compounds containing molybdenum, lanthanum and thorium :

Burn the weighed (3-5 mg) sample, mixed with ca. 20 mg of sodium carbonate in case of lanthanum and thorium, as usual using 500 ml Erlenmeyer Flask charged with 5 ml of 2*N* nitric acid or 10% ammonium hydroxide solution in case of Mo. Shake thoroughly for 2 minutes. Rinse the platinum gauze sample holder out using 10-15 ml of water. Boil the absorption solution gently for a few minutes to dissolve traces of the oxide. Determine the metal content as described below.

B. Precipitation of the metal-oxine complex :

(1) Immerse the tube containing the metal ion solution of Al(III), Cu(II), U(VI), Fe(III), La(III), Th(IV), or Mo(VI) in a water-bath adjusted at 70-80° (Use a boiling water-bath in case of Mo^{VI}). Add, with swirling, 2 ml of ammonium acetate followed by 1 ml of 1% oxine solution in acetic acid. Adjust the *p*H to about 7 with ammonia if necessary and 7.5 in case of La. After formation of the metal oxinate precipitate, allow the reaction medium to cool down slowly (For Mo, proceed directly with the hot solution to the next step).

(2) In case of Co(II), Ni(II) or Ti(IV) transfer the metal ion solution quantitatively to a 250-ml conical flask. Heat to about 50° then add, with constant stirring, 5 drops of acetic acid, 2 ml of ammonium acetate followed by 1 ml of 1% ethanolic oxine solution. Place the conical flask on a boiling water-bath for 10 minutes with a reflux condenser fitted at the mouth of the flask. Rinse the condenser with little water and allow the reaction medium to cool to room temperature.

C. Determination of the metal content :

Method I. Filter the metal-oxine complex, wash thoroughly with cold water (ca. 25 ml) until washings are colourless. Dry to constant weight (30-50 minutes) at 140° for Al, Cu, Fe, Mo, Co, La, at 110° for U, Ti, at 170° for Th, or at 230° for Ni.

Weigh and calculate the metal content on the basis of the following Formula AlQ_3, CuQ_2, FeQ_3, $MoO_2Q_2^{*a}$, CoQ_2, LaQ_3^{*b}, UO_2Q_2. HQ, $TiOQ_2$, ThQ_4^{*c} and NiQ_2 respectively where Q stands for the 8-hydroxyquinoline radical.

Method II. After filtration of the metal-oxine complex, receive the filtrate and washings in a 250 ml conical flask then add 5 ml of 5*N* hydrochloric acid followed by 1 ml of 10% potassium bromide. An accurately measured excess of potassium bromate solution is introduced, the flask is stoppered, shaken, and left in the dark for 5 minutes. Add 4 ml of 10% potassium inside and titrate the liberated iodine with 0.033 *N* sodium thiosulphate solution to the starch end point.

Method III. Dissolve the dried precipitate in 3 ml of conc. hydrochloric acid (in case of Mo, dissolve in the same volume of conc. sulphuric acid). Receive the dissolved metal oxinate in a 250 ml conical flask and determine the amount of released oxine exactly as described under Method II. In case of Fe, add 2-3 drops of 89% phosphoric acid before addition of the bromide solution. For copper oxinate, titrate the liberated Cu(II) iodometrically.

Results and Discussion

Of the reagents that have gained popularity in analytical work is 8-hydroxyquinoline. This is due to:

(1) Oxine precipitates almost every metal in the periodic table except the alkaline metals and, in low concentrations, the alkaline earth metals[8]. A character which offers great advantage in the analysis of organometallics. Selectivity of the reagent is not essential since organic compounds containing more than one metal are not abundant.

(2) Ability of oxine towards different methods of determination, e.g., gravimetric, titrimetric, spectrophotometric or polarographic.

(3) The metal oxinate precipitates are usually dried easily and weighed directly in the anhydrous form. The high conversion factor is quite favourable (1 mg each of):

AlQ_3 = 0.0856 mg Al; FeQ_3 = 0.1145 mg Fe; $TiOQ_2$ = 0.1360 mg Ti; NiQ_2 = 0.1692 mg Ni; CoQ_2 = 0.1697 mg Co; CuQ_2 = 0.1806 mg Cu; MoO_2Q_2 = 0.2305 mg Mo; UO_2Q_2. HQ = 0.3384 mg U; LaQ_3 = 0.2433 mg La and ThQ_4 = 0.2872 mg Th.

(4) The titrimetric determination of oxine depends on its bromination according to:

$$C_9H_7ON + 2\,Br_2 = C_9H_5ONBr_2 + 2HBr$$

TABLE 1—MICRODETERMINATION OF Al, Cu, Co, Ti, U, Ni, Fe, La, Th or Mo IN SOME OF THEIR ORGANOMETALLIC COMPOUNDS BY OPEN TUBE DECOMPOSITION

Compound	Sample Wt (mg)	Metal(%) Calc.	Found Method I	Found Method II	Found Method III	Error(%) I	Error(%) II	Error(%) III
Aluminium Oxinate	4.080	5.87	5.99	5.83	5.85	+0.07	−0.04	−0.02
	3.985		5.75	5.90	5.83	−0.12	+0.03	−0.04
Copper acetate	3.855	31.82	31.65	31.89	—	−0.17	+0.07	—
	4.450		31.84	31.81	—	+0.02	−0.01	—
Copper anthranilate	3.555	18.92	18.95	18.83	—	+0.03	−0.09	—
	3.260		19 00	19.02	—	+0.08	+0.10	—
Copper pyridine thiocyanate	4.625	18.80	18.78	18.91	—	−0.02	+0.11	—
	4.890		18.83	19.00	—	+0.03	+0.20	—
Cobalt anthranilate	3.450	17.79	18.08	18.03	17.75	+0.29	+0.24	−0.04
	4.155		17.72	17.82	17.94	−0.07	+0.08	+0.15
Potassium titanyl oxalate	3.245	13.96	13.92	13.98	13.99	−0.04	+0.02	+0.03
	4.360		14.02	13.79	14.01	+0.06	−0.17	+0.05
Uranyl acetate	3.005	56.13	56.31	56.22	56.01	+0.18	+0.09	−0.12
	3.100		55.74	55.96	55.98	−0.39	−0.17	−0.15
Nickel anthranilate	3.015	17.74	17.85	17.75	17.92	+0.11	+0.01	+0.18
	4.003		18.01	17.70	17.68	+0.27	−0.04	−0.06
Nickel tetrapyridine thiocyanate	3.935	11.95	11.84	11.92	11.99	−0.03	−0.03	+0.04
	3.983		11.91	12.02	11.85	+0.01	+0.07	−0.10
Ferric citrate	4.140	16.51	16.88	16.51	16.62	+0.21	−0.16	−0.05
	4.815		16.91	16.38	16.34	−0.16	−0.29	−0.33
	6.960		16 16	16.21	16.10	−0.51	−0.46	−0.57
Molybdenum oxinate	4.280	23.03	23.25	23.02	23.01	+0.18	−0.05	−0.06
	3.660		22.98	23.10	22.93	−0.09	+0.03	−0.14
	3.090		23.14	22.97	23.21	+0.07	−0.10	+0.14
Lanthanum oxinate	3.727	24.33	24.48	24.45	24.20	+0.15	+0.12	−0.13
	4.530		24.25	24.23	24 47	−0.08	−0.10	+0.14
	4.297		24.56	24.22	24.18	−0.23	−0.11	−0.45
Thorium oxinate	3.587	28.72	28.87	28.61	28.84	+0.15	−0.11	+0.12
	4.529		28.60	28.66	28.58	−0.12	−0.06	−0.14
	4.985		28.57	28.55	28.56	−0.15	−0.17	−0.16

TABLE 2—MICRODETERMINATION OF Mo, La AND Th IN SOME OF THEIR ORGANOMETALLIC COMPOUNDS BY THE OXYGEN FLASK COMBUSTION

Compound	Sample Wt (mg)	Metal				Error		
		Calc.	Found			I	II	III
			Method I	Method II	Method III			
Molybdenum oxinate	4.075	23.03	23.15	23.45	23.00	+0.12	+0.42	−0.03
			23.30	23.32	23.25	+0.27	+0.21	+0.22
			23.00	22.95	22.90	−0.03	−0.08	−0.13
Lanthanum oxinate		24.33	24.51	24.15	24.09	+0.28	−0.18	−0.24
			24.17	24.07	24.45	−0.16	−0.26	+0.12
			24.00	24.11	24.49	−0.33	−0.22	+0.16
Thorium oxalate		60.41	60.32	60.55	60.63	−0.09	+0.14	+0.22
			60.45	60.48	60.49	+0.04	+0.07	+0.08
			60.52	60.23	60.22	+0.11	−0.18	−0.19
Thorium oxinate		28.72	28.97	28.73	28.95	+0.25	+0.01	+0.23
			28.95	28.67	28.63	+0.23	−0.05	−0.09
			28.55	28.57	28.51	−0.17	−0.15	+0.21

Therefore, quinolinate salts of divalent cations require 8-equivalents of bromide and trivalent cations require 12-equivalents. Such amplification reaction allow high accuracy.

In the present work, the advantages of oxine have been utilized; the developed procedure applies the same reagent for analysis of the metals investigated and the per cent of the metal is estimated using both the gravimetric and the titrimetric methods. For the determinations carried out using Methods I-III, the average per cent error amounts to ± 0.15, ± 0.11 and ± 0.14 respectively (Table 1) and ± 0.23, ± 0.19 and ± 0.18 (Table 2). The proposed procedure is general for all of the metals studied. Precipitation of the oxinate is accomplished from solutions of *p*H of about 7. This *p*H value lies well within the *p*H range recommended for complete precipitation of any of the metals tested.

The satisfactory results given in Table 1 reflect the efficiency of the open tube method for decomposition of organometallics containing metals such as Al, Cu, U, Ti, Co, Fe, Ni, La, Th or Mo. Few drops of 3 : 1 nitric-perchloric acid mixture proved efficient for mineralizing the various metals tried. Within 5-10 minutes the decomposition is complete and the metal transferred in the nitrate form. In this respect, nitric acid is superior to sulphuric acid for analysing organic compounds.

The closed flask method, already used for mineralisation of Cd, Mg, U, Zn, Co, Mn, Ti, Cu, Pb, Al, Fe, Ni, Ca and Bi[3-5] has been extended for decomposition of organic compounds containing Mo, La and Th. The released metal ion is totally present as Mo(VI), La(III) or Th(IV).

Large numbers of samples have been analysed under routine conditions with good results.

Experience gained with the two methods of decomposition[3,6] suggests that, though both techniques are efficient for a wide variety of metals, the open tube method seems more convenient.

References

1. G. INGRAM, "Methods of Organic Elemental Microanalysis", 1st. Ed., pp. 265-381 Reinhold, New York, 1962.

2. W. SCHÖNINGER, *Microchim. Acta*, 1955, 123.

3. A. B. SAKLA, S. W. BISHARA and S. A. ABOU TALEB, *Microchem. J.*, 1972, **17**, 436.

4. A. B. SAKLA and S. A. ABOU TALEB, *Microchem. J.*, 1973, **18**, 502.

5. A. B. SAKLA, S. W. BISHARA and R. A. HASSAN, *Anal. Chim. Acta*, 1974, **73**, 209.

6. Y. TSUCHITANI, Y. TOMITA and K. UENO, *Talanta*, 1962, **9**, 1023.

7. R. G. W. HOLLINGSHEAD, "Oxine and its Derivatives", Vol. I-IV, London, Butterworths, 1954, (a) p. 480, (b) p. 294, (c) p. 467.

8. H. F. WALTON, "Principles and Methods of Chemical Analysis", New Delhi, Prentice-Hall of India, 1966, p. 94.

J. Indian Chem. Soc.,
Vol. LVII, January 1980, pp. 60-62

Spectrophotometric Studies on Scandium(III), Yttrium(III) and Lanthanum(III) Complexes with Dibenzoyl Methane

R. M. AWADALLAH

Chemistry Department, Faculty of Science, Aswan, Assiut University, A. R. Egypt

Manuscript received 16 March 1979, accepted 30 November 1979

The reaction of dibenzoylmethane (DBM) with scandium (Sc^{3+}), yttrium (Y^{3+}) and lanthanum (La^{3+}) is studied spectrophotometrically in the ultraviolet region. The results showed that Sc^{3+}, Y^{3+} and La^{3+} form complexes with measurable absorbance in buffer solutions of pH 9.52, 8.6 and 9.6 for Sc^{3+}-, Y^{3+}- and La^{3+}-DBM, respectively. The complexes formed have a metal : ligand ratio of 2 : 1, 1 : 1, 1 : 2, 1 : 3 and 1 : 4. The apparent formation constants, K_f of the Sc^{3+}-, Y^{3+}- and La^{3+}-DBM complexes are determined from the spectrophotometric results.

In the present investigation, the results of spectrophotometric measurements on the reaction of dibenzoylmethane with Sc^{3+}, Y^{3+} and La^{3+} are discussed.

THE reactivity of polynuclear (β-diketones) organic species coordinated to a central metal ion has been a point of considerable activity due to a minor perturbation of an organic π electron systems as a result of induced electron transfer (due to effect of the terminal aromatic groups on the chelating abilities of β-diketones).

Scandium, yttrium and lanthanum were determined photometrically as thoron complexes and gravimetrically as Sc_2O_3, Y_2O_3 and La_2O_3[1], and extracted as salicylates[2].

Experimental

Solutions :

Standard Solutions :

$1\times10^{-3}M$ of either Sc^{3+}, Y^{3+} and La^{3+} were prepared by dissolving the appropriate accurately weighed amount of the A.R. (99.9%) $Sc(NO_3)_3 \cdot 4H_2O$, $Y_2(SO_4)_3$ and $La(NO_3)_3 \cdot 6H_2O$ in twice distilled water. Reagent solution ; $2\times10^{-3}M$-DBM was prepared by dissolving an accurately weighed amount of the solid dibenzoylmethane in the requisite volume of absolute ethyl alcohol (BDH).

Buffer Solutions :

Oxalic, boric, succinic acids, sodium sulphate, borax and sodium carbonate buffers (Thiel, Schulz and Coch) of *p*H's 1.5-11 were prepared as given by Britton[3] and checked by the aid of Pye Unicam Model 290MK 2*p*H Meter.

Working Procedure :

The spectrophotometric measurements in the ultraviolet region were performed on the Pye Unicam SP8000 Ultraviolet Recording Spectrophotometer with matched silica cells, 1 cm light path. The solution was prepared by mixing the metal ion with the ligand solution mixed with buffer, using blank containing the same concentration of the ligand as the same as in the case of the test solutions of Sc^{3+}-, Y^{3+}- and La^{3+}-DBM.

Results and Discussion

When a solution of DBM is mixed with the metal ions (Sc^{3+}, Y^{3+} and La^{3+}) under investigation, a pale yellow colour yields. Some new bands are observed in the visible spectrum region compared to that of the ligand.

Spectrophotometric Measurements :

The absorption curves of Sc^{3+}-, Y^{3+}- and La^{3+}-dibenzoylmethide complexes are characterised by three absorption bands. On comparison of these spectra with that of the dibenzoylmethane, it is apparent that the addition of the metal ion causes shift in the band to lower wavelength (hypsochromic shift) while the second band of the ligand shifts to longer wavelength (bathochromic shift) and a new is developed. The band at shorter wavelength is due to the ligand not bonded to the metal ion whereas the long wavelength band is due to the complexed ligand. The longer band is due to an intramolecular charge transfer. The absorbance of the complexes is influenced by some factors which are confined briefly as follows :

(i) Effect of pH :

On using solutions of $1\times10^{-5}M$-Sc^{3+} and $2\times10^{-5}M$-DBM, $2\times10^{-5}M$-Y^{3+} and $4\times10^{-5}M$-DBM, and $1\times10^{-5}M$-La^{3+} and $3\times10^{-5}M$- DBM

in a series of buffer solutions of pH's 1.39-11.31, the spectral absorbance of the solutions increases with increasing pH until it reaches to maximum at $pH=9.52$ in case of Sc^{3+}-DBM ($\lambda_{max}=213$, 273 and 393 nm), $pH=8.6$ in case of Y^{3+}-DBM ($\lambda_{max}=218$, 270 and 380 nm) and $pH=9.6$ in case of La^{3+}-DBM ($\lambda_{max}=214$, 245 and 350 nm) complexes, thereafter it decreases. The increase of absorbance with pH may be due to increased formation of the complex, while the decrease of absorbance may be probably due to the formation of some sort of hydroxy complexes due to the competition between the ligand groups and OH^- ions (higher alkalinity of buffer solutions). The displacement of the ligand groups through OH^- ions proceeds in succession till the hydroxide or a basic salt is finally precipitated. This is evident from the turbidity which appears at higher pH values.

(ii) Effect of dibenzoylmethane concentration :

On maintaining the metal ion concentration unchanged at $1\times10^{-5}M$-Sc^{3+}, $3\times10^{-5}M$-Y^{3+} and 1×10^{-5} M-La^{3+}, while that of dibenzoylmethane (DBM) is varied from $2\times10^{-6}M$-$4.5\times10^{-5}M$ in case of Sc^{3+}, $1\times10^{-5}M$-$1\times10^{-4}M$ in case of Y^{3+} and $2\times10^{-6}M$-$3.2\times10^{-5}M$ in case of La^{3+}, the absorption spectra increase gradually with increasing DBM concentration then reaching to more or less constant value as a result of saturation (equilibrium) attainment.

(iii) Effect of metal ions concentration :

For studying this factor, constant concentration of dibenzoylmethane is employed equal to $1\times10^{-5}M$ in case of Sc^{3+}, $5\times10^{-5}M$ in case of Y^{3+} and $3\times10^{-5}M$ in case of La^{3+}, while that of the metal ion is varied from $4\times10^{-6}M$ to $4\times10^{-5}M$ in case of Sc^{3+}, $1\times10^{-5}M$ to $1.2\times^{-4}M$ in case of Y^{3+} and $4\times10^{-6}M$ to $4\times10^{-5}M$ in case of La^{3+}, the spectral absorbance increases as the metal ion concentration increases. The absorption spectra of the complexes comprise three bands with λ_{max} at 213, 273 and 293 nm in case of Sc^{3+}-DBM, 218, 270 and 380 nm in case of Y^{3+}-DBM, and 212, 278 and 345 nm in case of La^{3+}-DBM complexes. The addition of metal ions to the aqueous solution containing DBM leads to a slight shift in the $\pi\rightarrow\pi^*$ transition of the aromatic system ($\lambda=241$ and 347 nm). The behaviour of dibenzoylmethane for salt formation can support the opinion that the bonding between the metal ion and the ligand is, to a large extent, of an electrostatic nature.

Confirmity of Beer's Law :

Beer's law is valid for utilising dibenzoylmethane (DBM) as a chromogenic reagent for the microanalytical determination of the elements. However, the calculated K_f values are quite higher amounting to 9×10^5, 2.5×10^5 and 4.4×10^5 cm^2/mole for the Sc^{3+}-, Y^{3+}- and La^{3+}-DBM complexes, respectively. The higher values of extinction coefficient render the method of interest concerning the analysis of the metals, Sc(41.96-419.56 ppb), Y(17.78-533.42 ppb) and La (138.9-694.57 ppb).

The Stoichiometry of the Complexes :

The stoichiometry of the Sc^{3+}-, Y^{3+}- and La^{3+}-DBM complexes was studied in buffer solutions of pH's 9.52, 8.6 and 9.6 for Sc^{3+}-, Y^{3+}- and La^{3+}-DBM complexes applying the molar ratio[4], continuous variation[5], straight line[6], slope ratio[7] and limiting logarithmic[8] methods. The methods denote the existence of 2 : 1, 1 : 1, 1 : 2 and 1 : 3 complexes. The results obtained are tabulated in Table 1.

The Apparent Stability Constant :

The apparent formation constants of the complexes of Sc^{3+}-, Y^{3+}- and La^{3+}-DBM under investigation were determined from the results of the spectrophotometric measurements. With the molar ratio and continuous variation methods, the relation applied is :

$$K_f=\frac{(A/Am)}{[1-(A/Am)]^{(n+1)}.\ n^2.\ [L]^n}$$

TABLE 1—STOICHIOMETRY OF Sc^{3+}-, Y^{3+}- AND La^{3+}- DIBENZOYLMETHIDE COMPLEXES

Method	Complexes of		
	Sc^{3+}-DBM	Y^{3+}-DBM	La^{3+}-DBM
M.R.	2 : 1, 1 : 1, 1 : 2, 1 : 3	2 : 1, 1 : 1, 1 : 2, 1 : 3	2 : 1, 1 : 1, 1 : 2, 1 : 3, 1 : 4
C.V.	2 : 1, 1 : 1, 1 : 2	2 : 1, 1 : 1, 1 : 2, 1 : 3	2 : 1, 1 : 1, 1 : 2, 1 : 3
S.L.	1 : 1, 1 : 2, 1 : 3	2 : 1, 1 : 4	1 : 1, 1 : 2, 1 : 3, 1 : 4
S.R.	1 : 1, 1 : 2	1 : 1, 1 : 2	1 : 1, 1 : 3, 1 : 4
L.L.	1 : 2, 1 : 3	1 : 1, 1 : 3	1 : 1, 1 : 2, 1 : 3, 1 : 4

M.R.=molar ratio,
C.V.=continuous variation,
S.L.=straight line,
S.R.=slope ratio,
L.L.=limiting logarithmic.

where

K_f = apparent formation constant of the complex.

A = absorbance at a given ligand concentration, [L].

Am = limiting absorbance value.

n = stoichiometric ratio (number of ligand groups in the chelate molecule).

β in case of the straight line method can be determined from the relation :

$\beta = \log([M^{n+}].[L^{-}])/(\log A - \log V)$

in which V = volume of the mixed solution.

TABLE 2—APPARENT STABILITY CONSTANTS OF Sc^{3+}-, Y^{3+}- and La^{3+}-DBM COMPLEXES

Method	Ratio	K_f of chelates of		
		Sc^{3+}-DBM	Y^{3+}-DBM	La^{3+}-DBM
M.R.	2 : 1	5.52×10^{6}	0.6297×10^{6}	2.017×10^{6}
	1 : 1	9.567×10^{4}	2.14×10^{7}	
	1 : 2	1.185×10^{12}		0.465×10^{12}
	1 : 3	8.98×10^{17}	0.724×10^{17}	
	1 : 4			0.526×10^{24}
C.V.	2 : 1	3.819×10^{6}	0.1958×10^{6}	0.416×10^{6}
	1 : 1			4.278×10^{7}
	1 : 2	1.7×10^{13}	0.165×10^{12}	0.641×10^{12}
	1 : 3		2.22×10^{17}	3.706×10^{19}
S.L.	1 : 1	4.643×10^{6}		7.699×10^{7}
	1 : 2	2.156×10^{13}		6.048×10^{14}
	1 : 3	1.001×10^{20}		1.778×10^{22}
	1 : 4		2.688×10^{26}	

The data obtained are grouped in Table 2. The values obtained denote that the 1 : 3 complexes are more stable.

The reaction between Sc^{3+}, Y^{3+} and La^{3+} and dibenzoylmethane (DBM) lead to the formation of the 2 : 1, 1 : 1 and 1 : 4 complexes.

References

1. N. N. SENTYURINER, *Zh. Analit. Khim.*, 1962, **17**, 442.
2. B. N. SUDARIKOV, V. A. ZAYTSEV and Y. G. PUCHKOV, Nauch. Doklady Vysshei Shkoly, *Khim. i. Khim. Tekhnol.*, 1959, No. 1, 80-3.
3. H. T. S. BRITTON, "Hydrogen Ions", D. Van Nostrand Company, Inc., 4th Edition, Vol. 1, (1956).
4. E. H. YOE and A. L. JONES, *Ind. Eng. Chem.*, 1944, **16**, 111.
5. P. JOB, *Ann. Chem.*, 1935, **6**, 97.
6. E. I. ASMUS, *Z. Anal. Chem.*, 1960, **178**, 104.
7. A. E. HARVEY and D. L. MANNING, *J. Amer. Chem. Soc.*, 1950, **72**, 4448.
8. H. E. BENT and C. L. FRENCH, *J. Amer. Chem. Soc.*, 1941, **63**, 568.

J. Indian Chem. Soc.,
Vol. LVII, January 1980, pp. 63-66

The Use of the Rotating Pt-Electrode at Zero Applied E.M.F. for the Microdetermination of Monovalent Phosphorus in Hypophosphorous Acid or Hypophosphite

A. M. HAMMAM, K. A. IDRISS and Z. R. EL-KOMI
Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt

Manuscript received 29 August 1979, accepted 30 November 1979

An amperometric method is described for the microdetermination of monovalent phosphorus using the rotating Pt-electrode vs S.C.E. and zero applied e.m.f. It is based on oxidation of hypophosphorous acid and hypophosphite with $KMnO_4$ to phosphorous acid and phosphite respectively under the following conditions: Acidity 0.05-0.6 and 0.2-1.68 *N* H_2SO_4 for H_3PO_2 and NaH_2PO_2 respectively; NaF: 0.4-1.5%: amounts of P(I): 2.4 μg-2.1 mg and 5.4 μg-7.24 mg corresponding to hypophosphorous acid and hypophosphite respectively. The equivalence point is reproducible; the method is accurate and can be utilized at concentrations lower than that with the potentiometric method.

THE electrochemical oxidation of hypophosphite to phosphite was studied in presence of metal electrodes and the polarization curves were shifted in the cathodic direction by 0.2V[1]. Several titrimetric methods have been utilized for the determination of monovalent phosphorus[2-11]. The oxidation of P(I) with $KMnO_4$ in sulphuric acid medium was studied; the reaction was sluggish and results were unsatisfactory[11].

So far as the authors are aware, an amperometric and point has not been utilized for the microdetermination of monovalent phosphorus by oxidation with $KMnO_4$ in fluoride medium using the rotating Pt.-electrode vs S.C.E. as reference at zero applied e.m.f. The present work aimed at finding out the optimum conditions for such a method.

Experimental

Reagents :

Preparation of solutions : Potassium permanganate solutions were prepared by a method similar to that of Stamm[10] and standardized with sodium oxalate[12] (normality of permanganate solutions is based on valency change of Mn^{+7} to Mn^{+3}). Solutions of hypophosphorous acid and sodium hypophosphite (AnalaR grade) were prepared in bidistilled water and standardized according to recommended procedure[2]. Dilute solutions of permanganate and monovalent phosphorus were obtained by appropriate dilution. Other solutions including 2% sodium fluoride, 2-9 *N* sulfuric acid and 0.25 *N* copper sulfate were prepared from the AnalaR chemicals in bidistilled water.

Titration Procedure :

The amperometric titration assembly[13] used consisted of a beaker; rotating platinum electrode, agar bridge, saturated calomel electrode (S.C.E.) and microburette. The attainment of a steady diffusion current was maintained by rotating the platinum electrode at a constant speed of 600 r.p.m. The hypophosphorous acid or sodium hypophosphite solution was mixed with the appropriate amount of sulfuric acid; sodium fluoride and copper sulfate, completed to a known volume (usually 15 ml) with bidistilled water and titrated with $KMnO_4$. The diffusion current corrected for dilution was calculated and plotted against the volume of permanganate. The dilution correction is made by multiplying the current measured by a factor of $V+v/V$, where V is the original volume and v is the volume of titrant added.

Results

Effect of acidity. Table 1 and curves in Fig. 1, show the effect of acidity on the accuracy of the results. Good end points are obtained at acidities ranging from 0.05 to 0.6 and 0.2 to 1.68 *N* H_2SO_4 for hypophosphorous acid and hypophosphite, corresponding to oxidation to phosphorus acid and phosphite respectively. The earlier attainment of end point at higher acidities is due to partial reduction of permanganate to divalent manganese.

Effect of NaF concentration : Table 2, reveals that results concordant with the theoretical values and with error less than 1% are obtained on using 0.4-1.5% NaF in presence of 0.4 and 0.8 *N* H_2SO_4

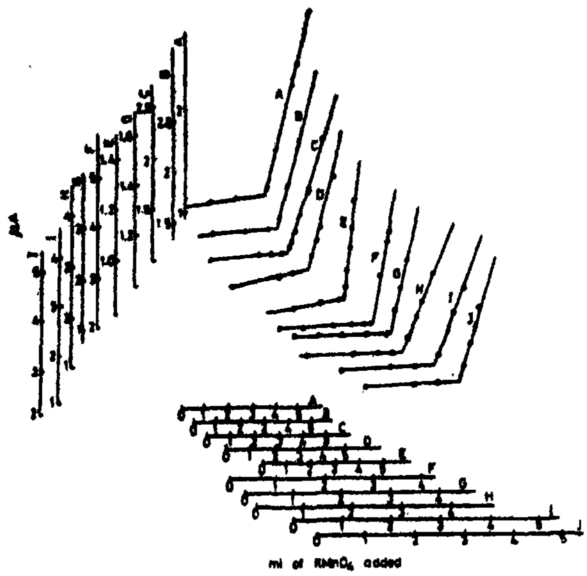


Fig. 1. Titration of 2.5 ml of 5.18×10^{-4} M H_3PO_2 with 7.95×10^{-4} N $KMnO_4$ in presence of 5 ml 2% NaF
(A) 0.07N H_2SO_4 ; (B) 0.1N H_2SO_4 ; (C) 0.3N H_2SO_4 ; (D) 0.8N H_2SO_4 ; (E) 1.2N H_2SO_4.

Titration of 5 ml of 1.17×10^{-4} M NaH_2PO_2 with 3.97×10^{-4} N $KMnO_4$ in presence of ml 2% NaF
(F) 0.42N H_2SO_4 , (G) 0.9N H_2SO_4 , (H) 1.2N H_2SO_4 ; (I) 1.68N H_2SO_4 ; (J) 2N H_2SO_4.

TABLE 1—EFFECT OF ACIDITY. TITRATION OF P(I) WITH $KMnO_4$ IN PRESENCE OF 5 ml 2% NaF AT DIFFERENT ACIDITIES (TOTAL VOLUME 15 ml)

Acidity NH_2SO_4	Volume of $KMnO_4$ consumed (ml)	Theoretical end point (ml)	Error (%)
Titration of 2.5 ml 5.17×10^{-4} M H_3PO_2 with 7.952×10^{-4} N $KMnO_4$			
0.07	3.28	3.26	0.67
0.10	3.27	3.26	0.36
0.30	3.26	3.26	Nil
0.80	3.24	3.26	0.55
1.20	3.22	3.26	1.16
Titration of 5 ml 1.16×10^{-4} M NaH_2PO_2 with 3.976×10^{-4} N $KMnO_4$			
0.42	2.96	2.94	0.61
0.90	2.95	2.94	0.27
1.20	2.95	2.94	0.27
1.68	2.92	2.94	0.68
2.00	2.90	2.94	1.36

TABLE 2—EFFECT OF NaF CONCENTRATION. TITRATION OF P(I) WITH $KMnO_4$ IN PRESENCE OF DIFFERENT VOLUMES OF 2% NaF. (TOTAL VOLUME 15 ml)

Volume of 2% NaF (ml)	Volume of $KMnO_4$ consumed (ml)	Theoretical end point (ml)	Error (%)
Titration of 2.5 ml 5.18×10^{-4} M H_3PO_2 with 7.952×10^{-4} N $KMnO_4$ (acidity 0.4N H_2SO_4)			
7.5	3.25	3.26	0.24
7.0	3.26	3.26	Nil
5.0	3.27	3.26	0.36
2.0	3.27	3.26	0.36
(Table 2 Contd.)			
Titration of 5 ml 1.17×10^{-4} M NaH_2PO_2 with 3.976×10^{-4} N $KMnO_4$ (acidity 0.8N H_2SO_4)			
7.5	2.94	2.94	Nil
6.0	2.93	2.94	0.34
5.0	2.93	2.94	0.34
2.0	2.92	2.94	0.68

in case of hypophosphorous acid and hypophosphite respectively.

Effect of concentration of monovalent phosphorus : Under the optimum conditions of acidity and F^- ions concentration, amperometric titration of hypophosphorous acid and/or hypophosphite with $KMnO_4$ is a satisfactory method for the determination of microamounts of reductants based on oxidation to phosphorus acid and/or phosphite respectively whereby permanganate is reduced to trivalent manganese (Table 3, Fig. 2). The method reveals the feasibility of determining amounts of monovalent phosphorus varying from 2.4 μg to 3.6 mg with fair accuracy.

TABLE 3—DETERMINATION OF DIFFERENT AMOUNTS OF MONOVALENT PHOSPHORUS, TITRATION WITH $KMnO_4$ IN PRESENCE OF 1% NaF

Sl. No.*	Monovalent Phosphorus (mg) Taken	Found	Error (%)	Standard** deviation (mg)	Total volume of solution (ml)
Titration of H_3PO_2 in presence of 0.4N H_2SO_4					
1.	2.008000	1.992000	0.67	0.0134	25
2.	0.200800	0.199800	0.49	0.0116	25
3.	0.040130	0.039900	0.57	0.0067	25
4.	0.040130	0.040020	0.27	0.0074	10
5.	0.008026	0.008040	0.17	0.0070	10
6.	0.004013	0.004027	0.34	0.0042	10
7.	0.002407	0.002426	0.78	0.0042	10
Titration of $H_2PO_2^{-1}$ in presence of 0.8N H_2SO_4					
8.	7.246000	7.188000	0.80	0.0244	25
9.	0.905700	0.910400	0.51	0.0201	25
10.	0.04528	0.045020	0.57	0.0068	25
11.	0.04528	0.04514	0.30	0.0059	10
12.	0.01087	0.01088	0.09	0.0046	10
13.	0.00906	0.00911	0.55	0.0068	10
14.	0.00543	0.00546	0.55	0.0050	10

* (1) 0.0259M H_3PO_2, 0.0397N $KMnO_4$; (2) 2.6×10^{-4} M H_3PO_2, 3.97×10^{-3} N $KMnO_4$; (3+4) 5.18×10^{-4} M H_3PO_2, 7.95×10^{-4} N $KMnO_4$; (5–7) 5.18×10^{-4} M H_3PO_2, 7.95×10^{-4} N $KMnO_4$; (8) 0.0584M NaH_2PO_2, 0.0793N $KMnO_4$; (9) 5.85×10^{-3} M NaH_2PO_2, 7.93×10^{-3} N $KMnO_4$; (10+11) 5.85×10^{-4} M NaH_2PO_2, 7.63×10^{-4} N $KMnO_4$; (12) 1.17×10^{-4} M NaH_2PO_2, 1.59×10^{-4} N $KMnO_4$; (13+14) 5.85×10^{-4} M NaH_2PO_2, 7.93×10^{-4} N $KMnO_4$.

** 10 single titrations for each concentration.

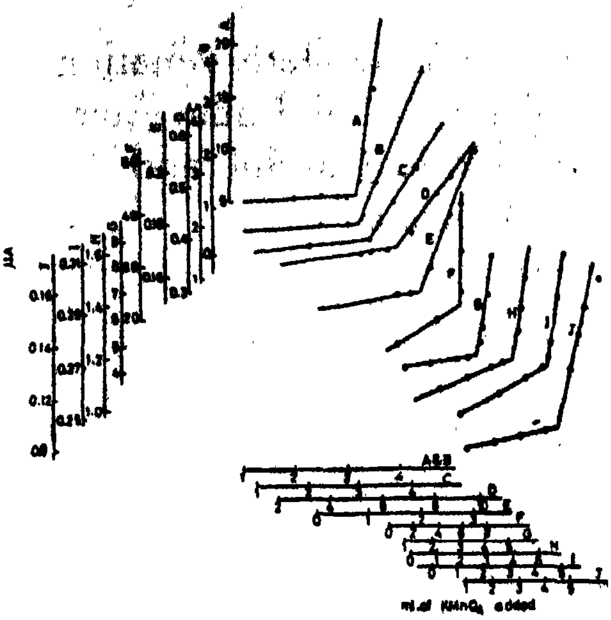


Fig. 2. Titration of H_3PO_2 (0.4$N H_2SO_4$) or NaH_2PO_2(3.0$N H_2SO_4$) with $KMnO_4$ in presence of 1% NaF.

	Total volume
(A) 2.5 ml 0.0250M H_3PO_2, 0.0397N $KMnO_4$	25
(B) 2.5 ml $5.18\times10^{-4}M$ H_3PO_2 ; $7.95\times10^{-4}N$ $KMnO_4$	25
(C) 2.5 ml $5.18\times10^{-4}M$ H_3PO_2 ; $7.95\times10^{-4}N$ $KMnO_4$	10
(D) 5 ml $5\times18\times10^{-5}M$ H_3PO_2 ; $7.95\times10^{-5}N$ $KMnO_4$	10
(E) 1.5 ml $5.18\times10^{-5}M$ H_3PO_2 ; $7.95\times10^{-5}N$ $KMnO_4$	10
(F) 4 ml 0.058M NaH_2PO_2 ; 0.0793N $KMnO_4$	25
(G) 2.5 ml $5.85\times10^{-4}M$ NaH_2PO_2 ; $7.68\times10^{-4}N$ $KMnO_4$	25
(H) 2.5 ml $5.85\times10^{-4}M$ NaH_2PO_2 ; $7.68\times10^{-4}N$ $KMnO_4$	10
(I) 3 ml $1.17\times10^{-4}M$ NaH_2PO_2 ; $1.59\times10^{-4}N$ $KMnO_4$	10
(J) 3 ml $5.85\times10^{-5}M$ NaH_2PO_2 ; $7.93\times10^{-5}N$ $KMnO_4$	10

Discussion

Hypophosphorous acid and hypophosphite are known to be oxidised quantitatively with $KMnO_4$ in acid solutions containing fluoride ions in presence of Cu^{+2} ions as catalyst and can be titrated either visually or potentiometrically to yield phosphorous acid and phosphite respectively as follows :

$$MnO_4^- + 2H_3PO_2 + 2HF_2^- + 2H^+ \rightleftharpoons MnF_4^- + 2H_3PO_3 + 2H_2O$$

$$MnO_4^- + 2H_2PO_2^- + 2HF_2^- \rightleftharpoons MnF_4^- + 2HPO_3^{-2} + 2H_2O$$

The practical importance of the amperometric titrations is due to their simplicity and rapidity. The equivalence point can be determined from few readings on each side of the end point whereas in the potentiometric titration, the equilibrium becomes sluggish as the concentration of the reactants decreases. In amperometric titration, it is not necessary to apply an external e.m.f. since $KMnO_4$ is reduced at almost zero applied e.m.f. as long as the solution contains reducible substances. Also, it is not necessary to deaerate the solutions before carrying out the titration because oxygen is not reduced under these conditions contrary to the case when titrations are carried out at more negative potentials. The titration curves are nearly reversed L-shaped curves and the intersection of the two branches of the curve gives the equivalence point which is reproducible. For quantitative determination, 10 samples between $5\times10^{-2}M$ and $5\times10^{-6}M$ concentrations of each reductant were selected and for every sample the titration was repeated ten times. The average error in the determination was well below $\pm1\%$. The amperometric method can be considered as a good analytical tool for microdetermination of P(I) and concentrations of hypophosphorous acid and hypophosphite corresponding to amounts of phosphorus ranging from 2.4 μg to 2.01 mg and from 5.4 μg to 3.62 mg respectively can be determined accurately.

References

1. V. S. Epifanova, Yu. V. Prusov and N. V. Flerov, *Electrokhimiya*, 1977, **13**, 1868.
2. R. I. Kaushik and O. P. Vermani, *Indian J. Chem.*, 1977, **15A**, 933-934.
3. M. V. Sastri and Kalidas, *Rec. Trav. Chim.*, 1955, **74**, 1045.
4. G. Gopal Rao and K. Bhaskara Rao, *Z. Anal. Chem.*, 1956, **150**, 333.
5. G. Pelizza and U. Risso, *Farmaco. Sci. Tec.*, 1946, **1**, 420.
6. G. Gopala Rao and H. S. Gowda, *Z. Anal. Chem.*, 1955, **146**, 167.
7. J. Cihalik *et al. Ceskoslov Farm.*, 1953, **2**, 8.
8. A. Schwicker, *Z. Anal. Chem.*, 1937, **110**, 161.
9. I. V. Hovorka, *Zechoslov. Chem. Comm*, 1930, **2**, 559.
10. H. Stamm, *Z. Angew. Chem.*, 1934, **47**, 791.
11. J. R. Pound, *J. Chem. Soc.*, 1942, 307.
12. R. M. Fowler and H. A. Bright, *J. Res. Nat. Bur. Standards*, 1935, **15**, 493.
13. I. M. Issa, M. A. Ghandour and A. M. Hammam, *J. Indian Chem. Soc.*, 1974, **51**, 872.

J. Indian Chem. Soc.,
Vol. LVII, January 1980, pp. 66-68

Solvent Extraction and Spectrophotometric Determination of Niobium and Tantalum-Quinizarin-3-Sulphonic Acid Complexes with Benzylamine, Dodecylamine and Tridecylamine in Benzene

R. M. AWADALLAH

Chemistry Department, Faculty of Science, Aswan, Assiut University, A. R. Egypt

Manuscript received 16 March 1979, accepted 30 November 1979

The study of the extraction of Nb^{5+}- or Ta^{5+}- QuS complex between benzylamine, dodecylamine or tridecylamine (in benzene) and aqueous solutions at pH 10.5 and 9 for Nb^{5+} and Ta^{5+}, respectively. The stepwise and overall extraction efficiency and distribution coefficient were calculated, after different time intervals and equilibration.

NIOBIUM and tantalum can be separated from each other and from accompanying elements, by liquid-liquid extraction of their complexes. The use of solvent extraction as a general method of separation in analytical chemistry has increased markedly in recent years as a powerful separation technique.

Benzylamine, dodecylamine and tridecylamine are liquid anion (baes) exchangers of high molecular weight amines (electrolytes), proving useful in chemical processing of extraction due to their ionic functional groups.

Niobium and or tantalum complexes with catechol[1,2], pyrogallol[3], dithiocarbamate derivatives[4,5,6] and 1, 2, 3, triphenylguanidine[7] can be extracted from weakly acid solutions employing *n*-butanol, ethyl acetate, chloroform and nitrobenzene as extractants.

Experimental

Solutions :

$5\times10^{-3}M-Nb^{5+}$ or Ta^{5+} was prepared by fusing the appropriate amount of Nb_2O_5 or Ta_2O_5 (A.R., 99.9%) with $K_2S_2O_7$(A.R.). The melt was dissolved in 20% tartaric acid solution[8].

$1\times10^{-3}M$-quinizarin-3-sulphonic acid solution was prepared by dissolving the required quantity of the dye in bidistilled water[9].

Boric, succinic, sodium sulphate, borax and sodium carbonate buffers of *p*H's 9 and 10.5, were prepared according to Thiel, Shulz and Coch[10].

Working Procedure :

The Nb^{5+}- and Ta^{5+}-QuS complexes ($[Nb^{5+}]=[Ta^{5+}]=3\times10^{-5}M$, $[QuS]=3\times10^{-4}M$) were prepared from buffer solutions of *p*H 10.5 and 9, and waiting for 40 and 30 min for maximum colour development of Nb^{5+} and Ta^{5+}, respectively[11,12]. Equal volumes of the complex and organic solvent (10 ml) were shaken together (using 60 ml separatory funnel) for a certain time. The phases separated were subjected to spectrophotometric measurements (using spectronic 20 spectrophotometer, 1.16 cm light path, Silica cell, Bausch & Lomb) for the study of the effect of solvent on λ_{max}, and on the absorption spectra of the complex. The effect of time of shaking on extraction efficiency was also studied. Multiple stage extraction was also performed, using small aliquots of the organic solvent (3, 4 and 3 mls) instead of the whole quantity at one time. In all cases, a blank solution containing the same concentration of ligand was used to compensate the absorbance due to ligand.

Calibration Graph :

For preparing the standard curve of Nb^{5+}-QuS complex, an aliquot of buffer solution of *p*H 10.5 was shaken with equal volume of organic solvent (benzylamine, dodecylamine and tridecylamine in benzene) for 1,5,6 and 7 minutes, whereas in case of Ta^{5+}-QuS complex, equal volumes of buffer solution of *p*H 9 and organic solvent (benzylamine, dodecylamine and tridecylamine) were shaken together for 1, 5 and 6 minutes. The aqueous phases saturated with these organic solvents were used in the preparation of the standard series of solutions of Nb^{5+} or Ta^{5+}-Qus using constant concentration of quinizarin and variable concentrations of Nb^{5+} or Ta^{5+} ranging from $1-5\times10^{-5}M$.

Results and Discussion

When Nb^{5+}-QuS solution is shaken with benzylamine and tridecylamine, λ_{max} (460 nm) is not affected, whereas that of Nb^{5+}-QuS with

TABLE 1—EXTRACTION EFFICIENCY AND DISTRIBUTION COEFFICIENT OF Nb^{5+}- AND Ta^{5+}- QuS COMPLEX ON USING 1% BENZYLAMINE IN BENZENE $[Nb^{5+}]=[Ta^{5+}]=3\times10^{-5}M$

(A) Nb^{5+}- QuS complex, $pH=10.5$, $\lambda=460$ nm. $[QuS]=1\times10^{-4}M$

Time in min	10	1	2	3	4	5	6	7	8	0*
A, in aq. ph.	0.486	0.320	0.366	0.384	0.436	0.450	0.485	0.485	0.485	0.510
$[Nb^{5+}]\times10^{-5}M$	3.0	0.60	0.5	0.35	0.425	0.35	0.15	0.15	0.15	3.0
$[Nb]\times10^{-7}g$	55.747	14.868	9.293	6.898	6.506	2.788	2.788	2.788	2.788	55.747
%X	—	26.67	16.67	11.67	14.17	11.67	4.90	4.90	4.90	—
$[Nb^{5+}]_o/[Nb^{5+}]_a$	—	0.364	0.200	0.132	0.165	0.132	0.052	0.052	0.052	—

o=absorbance of Nb^{5+}- QuS complex prepared in buffer shaken for 1 min with 1% benzylamine.
o*= " " " " " " " " " "

(B) Ta^{5+}-QuS complex, $pH=9$, $\lambda=460$ nm, $[QuS]=3\times10^{-4}M$

Time in min	0	1	2	3	4	5	6	7	8	0*
A, in aq. ph.	0.144	0.059	0.072	0.081	0.089	0.095	0.095	0.095	0.095	0.150
$[Ta^{5+}]\times10^{-5}M$	3.0	1.775	1.525	1.375	1.15	1.125	1.125	1.125	1.125	3.0
$[Ta^{5+}]\times10^{-7}g$	180.944	107.057	91.974	91.927	67.356	67.854	67.854	67.854	67.854	180.944
%X	—	59.17	50.83	45.83	38.33	36.67	36.67	36.67	36.67	—
$[Ta^{5+}]_o/[Ta^{5+}]_a$	—	1.449	1.045	0.846	0.622	0.579	0.579	0.579	0.579	—

o=absorbance of Ta^{5+}-QuS complex prepared in a buffer shaken for 1 min with 1% benzylamine.
o*= " " " " " " " " " " " " "
%X=Extraction efficiency.
A, in aq. ph.=Absorbance in aqueous phase.

TABLE 2—EXTRACTION EFFICIENCY AND DISTRIBUTION COEFFICIENT OF Nb^{5+}- AND Ta^{5+}- QuS COMPLEX ON USING 1% DODECYLAMINE IN BENZENE $[Nb^{5+}]=[Ta^{5+}]=3\times10^{-5}M$, $[QuS]=3\times10^{-4}M$

(A) Nb^{5+}-QuS complex, $pH=10.5$, $\lambda=440$ nm.

Time in min	0	1	2	3	4	5
A, in aq. ph.	0.145	0.000	0.031	0.059	0.000	0.000
$[Nb^{5+}]\times10^{-5}M$	3.0	3.0	2.36	1.78	3.0	3.0
$[Nb]\times10^{-7}g$	55.747	55.747	43.854	33.077	55.747	55.747
%X	—	100.0	78.62	59.31	100.0	100.0
$[Nb^{5+}]_o/[Nb^{5+}]_a$	—	1000.0	3.677	1.458	1000.0	1000.0

o=absorbance of Nb^{5+}-QuS complex prepared in a buffer solution shaken for 1 min with 1% dodecylamine in benzene.

(B) Ta^{5+}-QuS complex, $pH=9$.

Time in min	0	1	2	3
A, in aq. ph.	—	0	0	0
$[Ta^{5+}]\times10^{-5}M$	3.0	3.0	3.0	3.0
$[Ta]\times10^{-7}g$	180.9	180.944	180.944	180.944
%X	—	100	100	100
$[Ta^{5+}]_o/[Ta^{5+}]_a$	—	1000	1000	1000

TABLE 3—EXTRACTION EFFICIENCY AND DISTRIBUTION COEFFICIENT OF Nb^{5+}- AND Ta^{5+}- QuS COMPLEX ON USING 1% TRIDECYLAMINE IN BENZENE $[QuS]=3\times10^{-4}M$, $\lambda=460$ nm.

(A) Nb^{5+}-QuS complex, $[Nb^{5+}]=3\times10^{-5}M$, $pH=10.5$.

Time in min	0	1	2	3	4	5	6	7	8	0*
A, in aq. ph.	0.456	0.436	0.420	0.390	0.386	0.384	0.478	0.482	0.482	0.486
$[Nb^{5+}]\times10^{-5}M$	3.0	0.075	0.175	0.375	0.375	0.425	0.049	0.025	0.025	3.0
$[Nb]\times10^{-7}g$	55.747	1.394	3.25	6.968	7.431	7.898	0.911	0.465	0.465	55.747
%X	—	2.50	5.83	12.50	13.33	14.17	1.65	0.82	0.82	—
$[Nb^{5+}]_o/[Nb^{5+}]_a$	—	0.026	0.063	0.143	0.154	0.164	0.017	0.008	0.008	—

o=Absorbance of Nb^{5+}-QuS complex prepared in buffer shaken for 5 min with 1% tridecylamine
o*= " " " " " " " " " " "

(B) Ta^{5+}-QuS complex, $[Ta^{5+}]=2\times10^{-5}M$, $pH=9$.

Time in min	0	1	2	3	4	5	6	7	0
A, in aq. ph.	0.140	0.088	0.058	0.080	0.085	0.096	0.111	0.111	0.145
$[Ta^{5+}]\times10^{-5}M$	2.0	1.50	1.175	0.85	0.775	0.625	0.425	0.425	2.0
%X	—	75.0	58.75	42.50	38.75	31.25	21.25	21.25	—
$[Ta^{5+}]_o/[Ta^{5+}]_a$	—	3.0	1.424	0.739	0.633	0.455	0.27	0.27	—

dodecylamine is shifted to $\lambda=440$ nm (hypsochromic shift) due to the effect of solvent on λ_{max}. The Nb^{5+}-QuS complex in the dodecylamine layer gives maximum at $\lambda=520$. The results obtained are recorded in Tables 1, 2 and 3. The data reveal that the extraction efficiency and hence, distribution coefficient in case of tantalum are higher than that of niobium due to that the effective nuclear charge of tantalum is less than that of niobium and hence the acidity of tantalum is higher than that of niobium. Generally speaking, the percentage of extraction increases from benzylamine to dodecylamine due to that the electron density on the nitrogen atom of the amino group in dodecylamine (secondary aliphatic amine) is less than that of benzylamine (Primary aromatic amine) which proves well to attach to the central metal ion of Nb^{5+}- or Ta^{5+}-QuS complex through hydrogen bonding to take up all the complex into the organic phase (The solvent molecule participate directly in the formation of ion association complexes). The complete extraction with dodecyl amine may be also due to the sufficiently high dielectric constant that ions can exist in them, and their electron donor properties allow metal cations to be stabilised by solvation.

It is well established that dodecylamine is a powerful extractant than benzylamine and tridecylamine. Dodecylamine justifies all the requirements needed for a good extractant.

The lower values of the percentage of extraction and distribution coefficient of niobium and tantalum on using tridecylamine as extractant may be due to the effect of the steric hinderance of the methyl groups of the tertiary amine (tertiary branched chain amine), which may break the hydrogen bond established between the extractant and the complex compound.

References

1. F. V. Zaikovskii, *Zhur. Anal. Khim.*, 1956, **11**, 969.
2. F. V. Zaikovskii, *Zhur. Anal. Khim.*, 1956, **11**, 553.
3. J. A. Catoggio and L. B. Rogers, *Talanta*, 1962, **9**, 877.
4. H. A. Tyatina, V. B. Aleskovskii and A. D. Miller, Trudy leniger. Tekhnol. Inst. in. Lensoveta 48, 101 1958, Ref. *Zhur. Khim.*, 1959, 11, Abstr. No. 88, 317.
5. I. M. Gibalo, I. P. Alimarin and P. Davaadorzh, *Dokl, Akad. Nauk. SSSR*, 1963, **149**, 1326.
6. I. M. Gibalo, I. P. Alimarin and P. Davaadorzh, *Zhur. Anal. Khim.*, 1964, **19**, 467 ; 1963, **18**, 835 ; *Vesta. Mask gas, Univ. Ser. Khim.*, 1965, **4**, 73.
7. I. P. Alimarin and O. M. Petrukhin, *Zhur. Neorg. Khim.*, 1962, 7, 401 ; Ref *Zhur. Khim.*, 11, 1962, 21, Abstr. No. 21 D 57.
8. N. H. Furman, Standard Methods of Chemical Analysis, D. Van Nostrand Company Inc., Princeton, New Jersey, Toronto, New York, London, Vol. 1. The Elements, Sixth Edition, 1966.
9. J. Rosin, "Reagent Chemicals and Standards", D. Van Nostrand Company, Inc., Princeton, New Jersey, Toronto, London, Fifth Edition, 1967.
10. H. T. S. Britton, Hydrogen Ions, D. Van Nostrand Company, Inc., 4th Edition, Vol. 1, 1956.
11. I. M. Issa, R. M. Issa and R. M. Awadallah, *Egypt. J. Chem.*, 1975, **18**, No. 2, 211.
12. I. M. Issa, R. M. Issa and R. M. Awadallah, *Egypt. J. Chem.*, 1975, **18**, No. 5, 801.

J. Indian Chem. Soc.,
Vol. LVII, January 1980, pp. 69-72

Spectrophotometric Determination of Osmium and Ruthenium with N-Benzoyl-N′-Methylphenyl Selenourea

S. C. SHOME, M. MAZUMDAR and S. K. DAS

Chemical Laboratory, Presidency College, Calcutta-700 073 (India)

Manuscript received 20 May 1979, accepted 30 November 1979

N-benzoyl-N′-methylphenyl selenourea is recommended as a chelating agent for the spectrophotometric determination of osmium(VI) and ruthenium(III). It forms a wine red complex with osmium(VI) which can be quantitatively extracted with chloroform at *p*H 4.20-5.50. The reagent forms a reddish-brown complex with ruthenium(III). Quantitative extraction of ruthenium is obtained from a solution at 0.8*M*-3.0*M* hydrochloric acid. The chloroform extracts of both osmium and ruthenium complexes show maximum absorption at 460 nm and Beer's law is obeyed over the concentration ranging from 2.83 μg to 28.30 μg Os(VI)/ml and 0.65 to 9.81 μg Ru(III)/ml. The reagent *forms 2 : 1 and 3 : 1 complexes with osmium and ruthenium respectively.* The advantage of the use of N-benzoyl-N′-methylphenyl selenourea as a spectrophotometric reagent for both osmium and ruthenium lies in *the fact* that these metal ions can be determined in presence of all base metals and large excess of all other platinum metals. Simultaneous determination of osmium and ruthenium is possible with the chelating agent.

THIOUREA and several substituted thioureas[1-6] were used for the spectrophotometric determination of platinum metals. The platinum metals prefer the ligands having polarizable centre specially where back-bonding is possible. This condition favours selenium containing ligands which can be explained from the theoretical stand point. The dianion Se^{-2} (1.95 Å) would be more easily polarized because of its larger ionic radius than sulphur dianion S^{-2} (1.84 Å). Again, under favourable conditions the vacant 4d orbitals of selenium being probably of lower energy are suitable for back-bonding. Goddard[7] *et al* have determined the stability of metal complexes of selenourea, selenosemicarbazide as well as thiourea, thiosemicarbazide and found that selenium has greater affinity towards the class 'b' (platinum metals) than sulphur. Pilipenko and Sereda[8-10] first studied the analytical aspects of substituted selenoureas and selenoures for the determination of metals. Disubstituted selenoureas[11] have been introduced very recently as ligands for the platinum metals. In the present investigation N-benzoyl-N′-methylphenyl selenourea is introduced as a selective reagent for the determination and separation of micro amounts of osmium and ruthenium. It forms a wine red complex with osmium(VI) in hot acetate medium which can be fully extracted with chloroform at *p*H 4.20-5.50. Ruthenium(III) reacts with the reagent in hot dilute hydrochloric acid medium forming a reddish-brown complex which is quantitatively extracted with chloroform. The advantage of the use of N-benzoyl-N′-methylphenyl selenourea as a spectrophotometric reagent for osmium and ruthenium lies in the fact that these metal ions can be determined in the presence of all base metals and large excess of all other platinum metals. Simultaneous determination of osmium and ruthenium is also possible with this chelating agent.

Apparatus : A Carl-Zeiss spectrophotometer PMQII type equipped with one cm quartz cells was used for the transmittance measurements. All the *p*H measurements were carried out with a Cambridge *p*H meter (Bench model).

Reagent and Chemicals : Preparation and properties of N-benzoyl-N′-methylphenyl selenourea.

N-benzoyl-N′-methylphenyl selenourea was prepared by the following method as described by Douglass[12] : Benzoylisoselenocyanate was obtained by adding 0.1 mole benzoyl chloride to a solution of 0.1*M* mole of potassium selenocyanate in 200 ml of acetone. An exothermic reaction took place with the separation of potassium chloride, which was filtered. To the filtrate 0.1 mole of monomethyl aniline in 100 ml of acetone was added as rapidly as the vigorous boiling of the reaction mixture would permit. When the reaction had subsided, the mixture was poured slowly with stirring into 630-800 ml of cold water. The solid selenourea which separated was removed by filtration. The crude yellow mass was recrystallized several times from 50% ethanol using a small quantity of charcoal. N-benzoyl-N′-methylphenyl selenourea was thus obtained as pale yellow shining crystals (m.p. 120-121°). The compound is appreciably stable towards heat, light, air and non-oxidising acid. On prolonged exposure to air the compound exhibits reddish colour due to decomposition.

Reagent solution : A $0.01M$ solution of the reagent was prepared by dissolving a weighed amount of dried and recrystallized N-benzoyl-N′-methylphenyl selenourea in ethanol and the volume was made up to the mark by adding more ethanol.

Standard metal solutions : Osmic acid was dissolved in $0.1M$ sodium hydroxide and was standardized by precipitating the metal as sulphide, which was then ignited in a current of hydrogen to be weighed as metal. The standard solution of ruthenium was prepared by dissolving a weighed amount of the corresponding chloride in dilute hydrochloric acid and the metal content of the solution was determined by precipitating with thiosalicylamide[18]. Weaker solutions of the metals for the spectrophotometric determination were prepared by proper dilution of the stock solution. The solution of osmium was preserved in cold.

The standard solutions of the metals used to study the effect of diverse ions were prepared by dissolving weighed amounts of their salts in distilled water. Dilute hydrochloric acid was added where required. Solutions of anions were prepared from their respective alkali metal salts.

All the chemicals used were of A.R. grade.

Procedure :

Osmium : A known volume of the osmium solution containing about 250 μg of metal was placed in a 100 ml separatory funnel. The pH of the solution was adjusted between 4.20 and 5.50 by the addition of 10% sodium acetate solution and dilute hydrochloric acid. To this, 3 ml of reagent solution ($0.01M$) were added and thoroughly mixed. The mixture was warmed on a boiling water bath for 5 minutes. The wine red precipitate formed was extracted with chloroform. The total volume of the extract was made to 25 ml with chloroform and the absorbance of the solution was measured at 460 nm against a reagent blank prepared under similar conditions.

Ruthenium : A measured amount of the ruthenium solution was taken into a 100 ml separatory funnel and the solution was made $1M$-$3M$ in respect of hydrochloric acid. To this, 2 ml of the reagent solution ($0.01M$) were added and thoroughly mixed. The mixture was warmed on a boiling water bath for half an hour. The reddish brown precipitate was extracted with chloroform. The volume was made to 25 ml with chloroform and the absorbance was measured at 460 nm against the reagent blank.

Results and Discussion

Absorbance curves : The absorbance curves of the solutions of osmium and ruthenium complexes are shown in Fig. 1. The chloroform extracts of

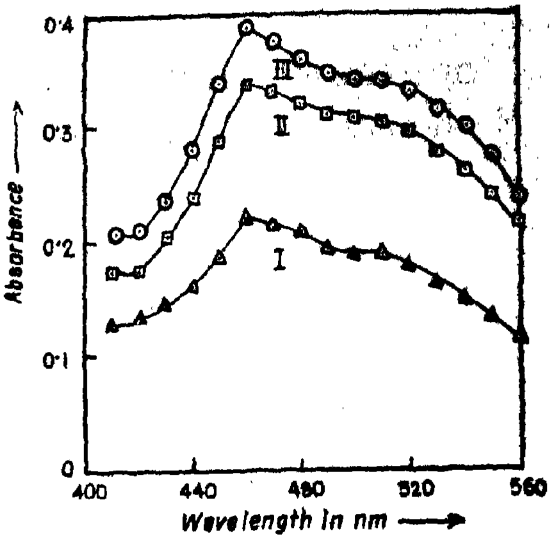


Fig. 1.1. Absorbance curves of Osmium-N-Benzoyl-N′-methylphenyl-selenourea complex in chloroform.
[Os] : I=3.08 μg/ml, II=6.16 μg/ml, III=7.70 μg/ml

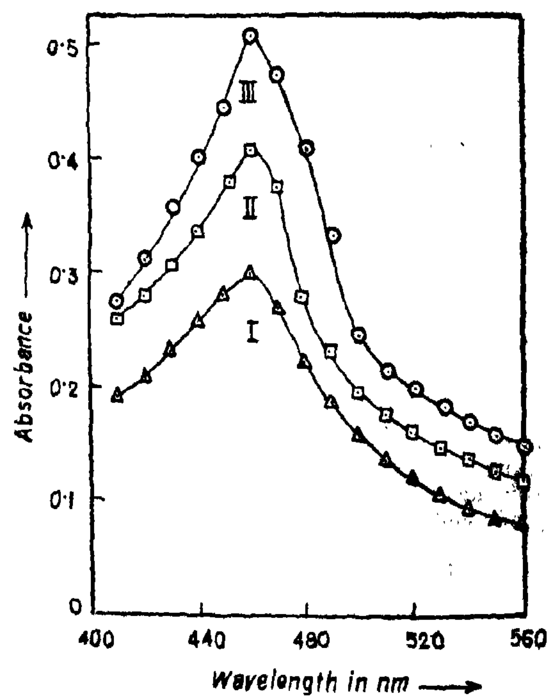


Fig. 1.2. Absorbance curves of Ruthenium-N-Benzoyl-N′-methylphenyl selenourea complex in Chloroform.
[Ru]: I=3.27 μg/ml, II=4.896 μg/ml, III=6.54 μg/ml

both osmium and ruthenium complexes show maximum absorbance at 460 nm, where the reagent has practically no absorption.

Effect of acidity : The acidities of the osmium and ruthenium solutions were adjusted by adding 10% sodium acetate solution and dilute hydrochloric

acid. After extraction of the metal complexes, the acidities of the aqueous layers were measured either by titrating against a standard alkali or with the aid of a pH meter. It was observed that ruthenium was completely extracted when the solution was 0.8-3.0M with respect to hydrochloric acid. The extraction of osmium was quantitative between pH 4.20 and 5.50.

Stability of colour : The colour of the chloroform extracts of the metal complexes was found to be stable for 24 hours, after which it slowly faded.

Conformity to Beer's law : It was observed that the Beer's law holds good at 460 nm over the concentration of osmium and ruthenium ranging from 2.83 μg ml^{-1} to 28.30 μg ml^{-1} and from 0.56 μg ml^{-1} to 9.81 μg ml^{-1} respectively.

Nature of metal complexes in solution : The empirical formulae of osmium and ruthenium complexes formed with N-benzoyl-N'-methylphenyl selenourea were determined by the mole-ratio method[14]. The results indicate that the chelating agent forms 2 : 1 and 3 : 1 complexes with osmium and ruthenium respectively. These compositions were verified by the slope-ratio method.

Sensitivity, Molar Extinction Co-efficient and Optimum Concentration range for Photometry of Osmium and Ruthenium : The sensitivities, molar extinction co-efficients of osmium and ruthenium complexes and optimum concentration ranges for the determination of these two metals are shown in Table 1.

TABLE 1—MOLAR EXTINCTION CO-EFFICIENT, SENSITIVITY AND OPTIMUM CONCENTRATION RANGE FOR PHOTOMETRY OF RUTHENIUM AND OSMIUM

Ruthenium				Osmium			
Wave length nm.	Molar extinction co-efficient l mole^{-1} cm^{-1}	Sensitivity μg cm^{-2}	Optimum concentration range in μg/ml	Wave length nm.	Molar extinction co-efficient l mole^{-1} cm^{-1}	Sensitivity μg cm^{-2}	Optimum concentration range in μg/ml
400	6.93×10^{3}	0.015	1.56-5.46	460	8.128×10^{3}	0.023	6.72-22.22

Effect of diverse ions :

Osmium(VI) and ruthenium(III) were determined with N-benzoyl-N'-methylphenyl selenourea in presence of known amounts of large numbers of diverse ions, following the procedure described above. Interferences of most of the base metals were avoided by using E.D.T.A. or tartrate. Interference of ruthenium in the determination of osmium was avoided by prior extraction of ruthenium at 2M hydrochloric acid. All the other platinum metals did not interfere with the determination

TABLE 2—EFFECT OF DIVERSE IONS IN THE SPECTROPHOTOMETRIC DETERMINATION OF OSMIUM(VI) AND RUTHENIUM(III)

Osmium (212.25 μg)		Ruthenium (183.40 μg)	
Diverse ions	Amount tolerated (μg)	Diverse ions	Amount tolerated (μg)
E.D.T.A.	5000	E.D.T.A.	5000
Tartrate	5000	Tartrate	5000
PO_4^{3-}	7000	PO_4^{3-}	7000
F^-	7000	F^-	7000
Mn^{2+}	1000^b	Mn^{2+}	1000
Ni^{2+}	1000^b	Ni^{2+}	1000
Co^{2+}	1000^b	Co^{2+}	1000
Cd^{2+}	1500^b	Cd^{2+}	1500
Zn^{2+}	2000^b	Zn^{2+}	2000
Fe^{3+}	2000^a	Fe^{3+}	2000
Al^{3+}	1000^b	Al^{3+}	1500
Cr^{3+}	1000^b	Cr^{3+}	1000
Mo^{6+}	1000^b	Mo^{6+}	1000
W^{6+}	1000^b	Wo^{6+}	1000
Ti^{4+}	600^c	Ti^{4+}	1000
U^{6+}	1000	UO_2^{2+}	800
Ga^{3+}	1500^b	Ga^{3+}	1000
Th^{4+}	1000^b	Th^{4+}	1000
Cu^{2+}	1500^d	Cu^{2+}	1500
Rh^{3+}	375	Rh^{3+}	800
Pd^{2+}	1000	Pd^{2+}	100
Au^{3+}	1000	Au^{3+}	100
Pt^{4+}	750	Pt^{4+}	75
Ru^{3+}	917	Os^{8+}	825

^{a}=In presence of phosphate ions. ^{c}=In presence of fluoride ions.
^{b}=In presence of tartrate ions. ^{d}=In presence of EDTA.

of osmium or ruthenium. The tolerance limits for the various diverse ions as given in Table 2, represent the concentration of foreign ions in presence of which the transmittance of the extracts of the metal complexes was within ±2%.

Simultaneous determination of osmium and ruthenium in a mixture :

A mixture containing 212.25 μg of osmium(VI) and 183.40 μg of ruthenium(III) was taken in a 100 ml separatory funnel. The acidity of the mixture was then adjusted to 1-2 M with respect of hydrochloric acid, 2 ml of 0.01 M ethanolic solution of N-benzoyl-N'-methylphenyl selenourea were added and ruthenium was determined as described in the procedure. The pH of the aqueous layer was then adjusted to 5. To this 3 ml of 0.01 M reagent solution were added and osmium was determined as described above.

Accuracy and precision :

The relative mean errors and relative standard deviations for the determination of osmium and ruthenium at different concentrations of the metals are shown in Table 3. The results were obtained from sets of ten experiments under optimum conditions.

TABLE 8—ACCURACY AND PRECISION

Metal ion taken $\mu g\ ml^{-1}$	Metal ion found* $\mu g\ ml^{-1}$	Relative mean error%	Relative standard deviation %
Ruthenium(III)			
(1) 2.20	2.21	+0.45%	0.66%
(2) 8.07	8.06	−0.27%	0.90%
Osmium			
(1) 6.02	6.00	−0.33%	0.88%
(2) 12.04	12.07	+0.25%	0.66%

* Average of ten measurements under identical conditions.

Acknowledgement

The authors are indebted to Dr. H. R. Das, Assistant Professor of Chemistry, Presidency College for helpful discussion.

References

1. W. NIELSCH, *Micro. Chim. Acta.*, 1954, 532.
2. S. KOMATSU and K. TAKI, *Nippon Kagaku Zasshi.*, 1959, **80**, 397.
3. S. KOMATSU and K. ONISHI, *J. Chem. Soc., Japan*, 1955, **76**, 661.
4. E. B. SANDELL, Colorimetric Determination of Traces of Metals : 3rd Ed., New York, Interscience, 1959, p. 77.
5. S. B. KNIGHT, R. L. PARKS, S. C. LEIDT and K. L. PARKS, *Analyt. Chem.*, 1959, **29**, 571-4.
6. L. TSCHUGAEFF, *C. R. Acad. Sci. Paris*, 1918, **167**, 235.
7. D. R. GODDARD, S. O. AJAYA and M. J. CAMPBELL, *J. Chem. Soc.* A, 1969, 506.
8. A. T. PILIPENKO and I. P. SEREDA, *Zh. Anal. Khim.*, 1958, **13**, 3.
9. A. T. PILIPENKO and I. P. SEREDA, *Zh. Anal. Khim.*, 1961, **16**, 73.
10. A. T. PILIPENKO and I. P. SEREDA, *Zh. Neorg. Khim.*, 1961, **6**, 413.
11. DENIEL L. KLAYMAN and WOLFGANG H. H. GIINTHER, Organic Selenium Compounds. Their Chemistry and Biology, Wiley-Interscience, New York, 1973, p. 289.
12. I. B. DOUGLASS, *J. Amer. Chem. Soc.*, 1937, **59**, 740.
13. K. SUR and S. C. SHOME, *Anal. Chim. Acta.*, 1969, **48**, 145-153.
14. A. S. MAYER and G. H. AYRE, *J. Amer. Chem. Soc.*, 1957, **79**, 49.

J. Indian Chem. Soc.,
Vol. LVII, January 1980, pp. 73-75

Electrometric Studies on Clay-humic Acid Interactions

M. ADHIKARI and T. K. MUKHERJEE

Department of Applied Chemistry, Calcutta University

Manuscript received 25 February 1977, accepted 9 January 1980,

The interactions between H-clays (original and oxide-free) and humic acid fraction (HA) of soil humus have been studied by electrometric titrations.

Conductometric studies show the formation of four different types of complexes with original clay and three different types with clay (oxide-free) fractions. Potentiometric studies support these findings.

IT is an established fact that soil organic matter fractions are capable of interacting with clays to form complexes. Mechanisms of such reactions have been reviewed by Mortland[1] and Greenland[2].

In the present paper some attempts have been made to give information on the nature of interactions between clay and humic acid fractions employing electrometric methods.

Experimental

Organic matter was extracted and fractionated from Bigra Pond Sediment, Dist. Burdwan, W.B (0-15 cm depth) by the procedure adopted by Banerjee and Mukherjee[3]. The humic acid (HA) thus fractionated was dialysed and finally electrodialysed.

After removal of organic matter from the sediment, it was treated with H_2O_2 to remove the residual organic matter. The excess H_2O_2 was removed by warming it to 80-90° in water bath. The clay-fractions ($<2\mu$) were collected from this by the usual process of dispersion and sedimentation. The clay isolated was treated with dil HCl to convert it to H-clay which was then purified by dialysis. Finally these dialysed H-clay materials were shaken with a cation exchange resin (Amberlite I-R-120 in the H-form) to get the H-clay. For preparation of oxide-free clay, the procedure as adopted by Mehra and Jackson[4] was followed which was subsequently converted in H-form.

Conductometric Titration: In a number of stoppered 10 ml volumetric flasks, fixed amount of clay and increasing amounts of HA solutions were added. The contents of these flasks were shaken for 12 hrs and allowed to equilibrate for 7-8 days. The total volume was made up to 10 ml in each case. After equilibrium conductances of the solutions were measured by Leeds-Northrup conductivity bridge at 30°±0.5°. Conductometric titrations of HA fraction and HA-clay combinations with NaOH were also carried out.

Potentiometric Titration: Compositions of the complexes were determined from the inflexion points of conductometric titration curves as shown in Fig. 1(a). From this knowledge different complex species were prepared by mixing clay and HA in different complex species were prepared by mixing clay and HA in different mole ratios. These were titrated with NaOH solution in Cambridge *p*H-meter at 30°±0.5°.

The conductometric and potentiometric titration curves of H-clay-HA, H-clay (oxide-free)-HA and their complexes are shown in Figs. 1(b, c, d and e).

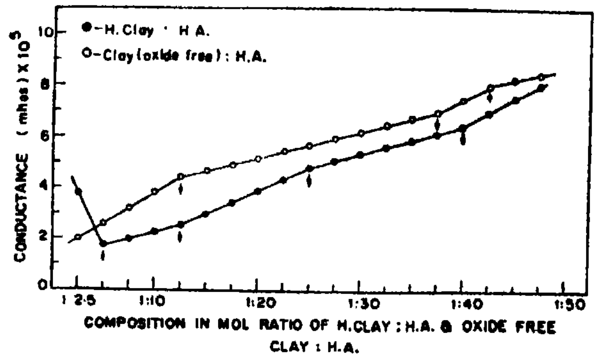


Fig. 1(a).

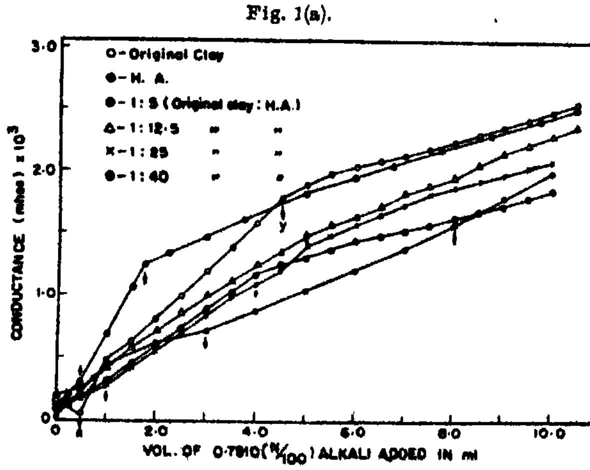


Fig. 1(b)

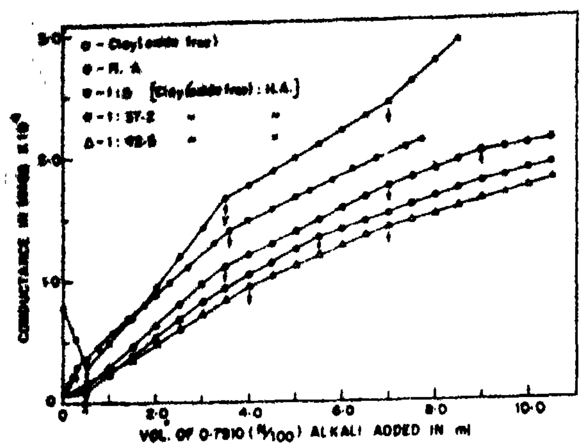


Fig. 1(c).

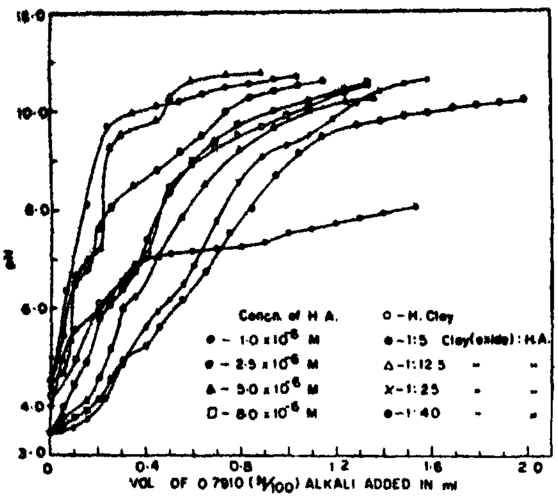


Fig. 1(d).

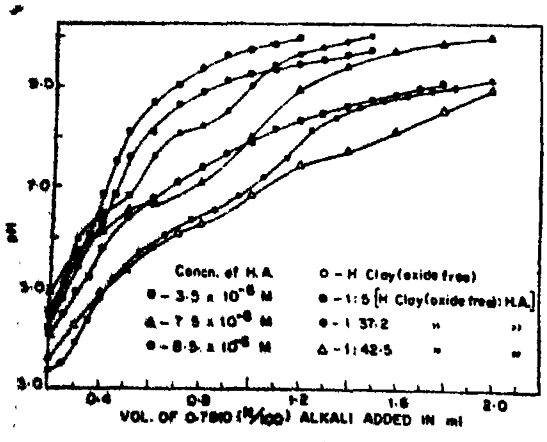


Fig. 1(e).

Results and Discussion

The average molecular weight of the electrodialysed HA and the clay were found by electrometric method[8] to be 2,000 and 30,000 respectively. The present discussions are based on such results.

Instantaneous conductometric titrations (curve not shown) of HA with H-clay (original and oxide-free) are of continuous nature showing no complex formation. But discontinuous titration (after equilibration), shows four inflexion points for original clay-HA and three for clay (oxide-free)-HA titrations, indicating complex formation at these points, Fig. 1(a). The molal compositions corresponding to the original clay-HA are 1 : 5, 1 : 12.5, 1 : 25 and 1 : 40 and clay (oxide-free)-HA are 1 : 5, 1 : 37.2 and 1 : 42.5 respectively.

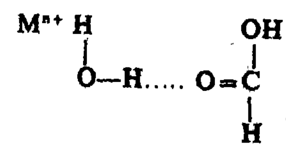
The conductometric titration of HA by caustic alkali show two breaks [Fig. 1(b)]. It also follows from conductometric titration of clay-HA system, the conductance of the solution depends on the number, the charge and the mobility of the ions present. Some of the characteristic points from the conductometric titration curves of clay-HA system can be described as follows :

(1) The low conductance at the point X [Fig. 1(b and e)] is attributable to the neutralization of hydroxyl ions by the H^+ ions which had previously been adsorbed in the clay-HA system. The very low dissociation of the cation from polyanion complex also contributes to the observation of very low conductance value.

(2) At the point Y [Fig. 1(b and e)] the conductivity of the "free base" determines the further course of the titration curve with a constant slope.

It also appears from conductometric titration systems, the adsorption of HA on clay-surfaces depends on cleavage of the hydrogen-bridge linkage between carboxyl and hydroxyl groups of the adjacent molecules of humic acids and more the adsorption the clay-HA systems tend to disperse. This corroborates with the view of Halla and Ruston[6].

The distinctive nature of conductometric titration curves of original clay, clay (oxide-free) and their complexes with HA indicate that sesqui-oxides present in soil clays play important role in the interaction between clays and organic compounds. From the increasing trend of conductance values of clay-HA complexes with caustic alkali, it may be inferred that there is a possibility of formation of 'water-bridge like compounds'[1] linking polymeric HA molecules to the exchangeable metal cations of the clay surface as :



where M^{n+} is the metal cation and –COOH is one of the functional groups of HA. On interaction with NaOH, Na^+ exchanges for polyvalent ions, such as Ca^{+2}, Mg^{+2}, Fe^{+3} etc., present on the clay surface. A fresh claysol-HA product does not show any distinct change in conductance measurements but the product on ageing actually changes to H-Al-clay system[7,8].

Potentiometric titration curve of HA, original clay-HA complexes with standard alkali are shown in Fig. 1(d and e). During the titration of original clay with NaOH, the change of *p*H is initially slow, indicating an weak acidity. But after that, the nature of the curve begins to flatten. This may be due to accumulation of osmotically active Na^+ ions in the mobile double layer of the clay surface, replacing the surface H^+ ions of the clay.

From the Fig. 1(d and e) it is seen that the lesser amounts of alkali is required for neutralization of HA than is needed to titrate clay-organic complexes which is due to uncoiling (unfolding) effect of HA after adsorption on clay surfaces, necessiating more alkali for neutralization of active groups. Similar observation was made by Alexandrova[9] in studying metal HA chelates as stated in Gieseking[10].

In order to get an idea about the mechanism of clay-HA interactions, the number of proton released from organic matter by addition of clay are assessed and shown in Table 1. From the data given in Table 1, it is evident that the number of protons released from organic matter increases with *p*H in all the clay-HA systems.

TABLE 1—NUMBER OF PROTONS RELEASED FROM HA/mole OF CLAY ADDED

*p*H	H-clay : HA complexes in mole ratio			
	1 : 5	1 : 12.5	1 : 25	1 : 40
4.0	0.22	0.24	0.5	0.27
4.5	0.26	0.34	0.52	0.28
5.0	0.32	0.38	0.58	0.32
5.5	0.36	0.42	0.74	0.58
6.0	0.52	0.48	0.90	0.60
6.5	0.58	0.52	0.92	0.62
7.0	0.62	0.56	0.94	0.66
7.5	0.64	0.60	1.08	0.72
8.0	0.76	0.64	1.16	0.80
8.5	0.82	0.70	1.28	0.86
9.0	1.02	—	1.56	0.92
9.5	1.10	—	1.60	1.04
10.0	—	0.86	1.80	1.20

It is thus evident that higher the concentration of organic matter, greater is the number of protons released and the maximum number of protons released is approximately 2 in the case of complex having molar composition of clay : HA = 1 : 25.

From this study it is inferred that clay-HA complexes are more or less stable up to a *p*H 7 to 8 and above which they begin to break up, resulting in release of larger number of protons[11]. It is noticed that in both clay (oxide) and clay (oxide-free)-HA complexes number of proton released at lower *p*H ranges is much less than unity in most cases.

Hence it may be inferred that HA may have penetrated into the co-ordination shell of the surface hydroxyl layer of the clay in such a way that it is not sensitive to *p*H change. Similar views were expressed by Edward and Bremner[12].

Furthermore, from the *p*H titration it appears that the nature of the curves are alike at the lower *p*H-range, irrespective of nature of clay system used, i.e., original or oxide-free. At *p*H 3.5 the differences of the titration properties of the clay ions are small, because at this *p*H-value the clay ions are still in a undissociated state in solution.

It is thus concluded that the linkage between HA and clay ions is of covalent character or formation of water bridge like compounds[1] which conforms to the views of Van Dijk[13], Khanna and Stevenson[14].

Acknowledgement

One of the authors (T.K.M.) is grateful to C.S.I.R., New Delhi for the award of Senior Research Fellowship.

References

1. M. M. MORTLAND, *Adv. Agron.*, 1970, **22**, 75.
2. D. J. GREENLAND, *Soil Sci.*, 1971, **111**, 34.
3. S. K. BANERJEE and S. K. MUKHERJEE, *J. Indian Soc. Soil Sci.*, 1972, **20**, 13.
4. O. P. MEHRA and M. L. JACKSON, *Clay & Clay Miner*, 1960, **7**, 317.
5. C. DUTTA, D.Phil. Thesis, Calcutta University, 1968.
6. MARTIN and REEVE, *J. Soil Sci.*, 1958, **9**, 89-100.
7. H. PAVAR and C. E. MARSHALL, *J. Soc. Chem. Ind.*, 1934, **53**, 750.
8. N. MUKHERJEE, B. CHATTERJEE and A. ROY, *Journal of Colloid Sci.*, N. Y., 1948, **3**, 437.
9. L. N. ALEXANDROVA, *Soviet Soil Sci.*, 1967, **7**, 903-913.
10. JOHN E. GIESEKING, *Soil Components*, 1975.
11. K. KAWAGUCHI and K. KYUMA, *Soil Plant Food*, 1959, **5**, 54.
12. C. A. EDWARD and J. M. BREMNER, *J. Soil Sci.*, 1967, **18**, 64.
13. VAN H. DIJK, *Sci. Proc. Roy. Dubl. Soc. Ser.*, 1960, A1, 163; Torf Kolloquium, Peat-Colloquium in Rostock, Deutsche Demokratische Republik, Poland 1967, 1/3.
14. S. S. KHANNA and F. J. STEVENSON, *Soil Sci.*, 1962, **93**, 298-305.

J. Indian Chem. Soc.,
Vol. LVII, January 1980, pp. 76-79

Thermochemistry of Copper(II)-Glycinate in tert-Butanol-Water and Glycerol-Water Mixtures at 25°

S. BANDOPADHYAY and S. ADITYA

Department of Applied Chemistry, Calcutta University, Calcutta-700 009, India

Manuscript received 31 August 1979, accepted 31 December 1979

The enthalpies of formation of the Cu(II)-glycinate in water and mixed solvents such as tert-butanol-water and glycerol-water media at 25° have been determined by calorimetry. The entropy-change and the free energy change in water have been calculated using the values of stability constant from literature. Results have been interpreted in terms of "structure-breaking" and "structure-making" effect. The role of solvents on the thermodynamic parameters has been discussed.

AMINO acids form complexes with metal ions in solution. They are of great importance in biochemical processes, since they have been used as model compounds for understanding the thermodynamic behaviour of proteins. Nozaki and Tanford[1] measured the solubilities of several amino acids in water and other solvents in order to evaluate the standard free energy contributions of non-polar groups of the conformational stability of proteins. Question arises concerning the detailed structure and reactions of ribonucleic acid, deoxyribonucleic acid, and their constituent base, sugar and phosphate units. Answering of these questions requires a knowledge of the sites and thermodynamic quantities associated with the interaction of protons and metal ions with these substances.

Co-ordination of an amino acid $H_2N(CH_2)_x$-COOH takes place through the amino nitrogen and the carboxylic group (generally as the carboxylate ion) according to the following reaction :

$$M^{n+} + nL^- \longrightarrow [ML_n] - (n-2)$$

Various thermodynamic data are available for the formation of transition metal complexes of amino acids in aqueous medium. Thornton and Skinner[2] determined the enthalpies of reactions of Cu(II), Ni(II), Zn(II) with glycine, serine, threonine and histidine in water. Stack and Skinner[3] determined the heats of formation of chelates of Cu(II), Ni(II), Co(II) and Zn(II) with glycine in water. Gergely, Nagypal and Sovago[4] have determined the thermodynamics of Co(II), Ni(II), Cu(II), Zn(II) with glycine and of Cu(II) with serine and threonine in aqueous medium. The complexes of amino acids with transition metals have been studied by various methods[5-11]."Calorimetry", "Potentiometry" "pH-metry" and "temperature coefficient methods". Although studies on the complexes of Co(II), Ni(II), Zn(II) and especially Cu(II) in aqueous medium have received much attention, knowledge of the thermodynamic data in mixed solvents are still lacking. Such studies will throw light on the solvent effects—solute-solvent, solvent-solvent interactions on the thermodynamic parameters.

In this communication we report the thermodynamic parameters of Cu(II)-glycinate in water at 25°, and the enthalpy of formation of Cu(II)-glycinate in tert-butanol-water and glycerol-water media at 25°.

Experimental

Glycerol and tert-butanol were purified by methods described in an earlier communication[12]. Copper sulphate solution was prepared by weighing directly $CuSO_4.5H_2O$ (B.D.H.-A.R.) and dissolving in a known quantity of $HClO_4$. The purity was checked by estimating the copper content by iodometry. The solution was used within several hours. Glycine (E. Merck-G.R.) was dried at 110° for one hour. It was then dissolved in a calculated quantity of NaOH solution to form sodium glycinate. The reacting solutions were taken in the same mixed solvent.

Perchloric acid and caustic soda were of analar grade and estimated in the usual way. All solutions were made with double-distilled water from an all-glass distilling set.

The details of the calorimeter used have been reported earlier[13]. Some modifications have been made, the bridge now being energized by a stabilized power supply. For calibration also a stabilized power source is used.

For the measurement of the enthalpy change of Cu(II)-glycinate in water, 5 ml of freshly prepared $CuSO_4$ solution (concentration ranging between 0.2-0.25*M*) in $HClO_4$ was taken in a glass bulb and 250 ml of large excess of glycine (concentration ~0.15*M*) in NaOH was taken in the Dewar flask. Both were taken in aqueous medium.

For the measurement of enthalpy change of formation of Cu(II)-glycinate in glycerol-water medium, concentration of $CuSO_4$ were taken between $(2.6\text{-}4.3) \times 10^{-3} M$ and concentration of glycine was taken $\sim 2 \times 10^{-2} M$, whereas in tert-butanol-water medium concentrations of $CuSO_4$ were taken between $(1.3\text{-}1.85) \times 10^{-3} M$ and that of glycine $\sim 1 \times 10^{-2} M$. Both solutions were prepared in the same mixed solvent. Calculated amount of NaOH solution of known strength was taken so as to maintain the final pH of the solution between 9.7-12. Concentration of glycine was always more than ten times the concentration of Cu^{++} ion.

Results

Since a small amount of Cu^{++} is reacted with large excess of glycine in the pH range 9.7-12, we get the enthalpy change for 1 : 2 type of complex[3]. Two reactions occur simultaneously,

$$Cu^{++} + 2A^- \rightleftharpoons CuA_2 \quad \cdots \quad (1)$$

$$H^+ + OH^- \rightleftharpoons H_2O \quad \cdots \quad (2)$$

(where HA stands for glycine)

From the total heat liberated (Q_1), we can get ΔH for reaction (1) after correction for liberation of heat, (Q_2), due to reaction (2) using the relation

$$\Delta H = -\frac{Q}{x}$$

where Q ($=Q_1\text{-}Q_2$) is the liberated heat in calories for x moles of CuA_2 formed.

We have used fairly dilute solutions, $[Cu^{++}] \simeq 10^{-3} M$ and all the Cu^{++} ions is complexed in the reaction. For different concentration of Cu^{++} ion and over a range of pH 9.85-12 of the solution after reaction we note that ΔH is the same within experimental error. So we have taken the experimental ΔH as ΔH°. The stability constant of Cu-glycinate has been determined by Gergely and coworkers[4]. Using this value, ΔG° and ΔH° in water at 25° are calculated from the relations :

$$\Delta G^\circ = -RT \ln K$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

Results are shown in Tables 1 and 2.

The values of the stability constants in tert-butanol-water and glycerol-water media are not available in literature. So ΔG° and ΔS° in the mixed solvents could not be calculated.

TABLE 1—THERMODYNAMIC PARAMETERS FOR $Cu^{++} + 2A^- \rightleftharpoons CuA_2$ IN WATER AT 25°C

No. of obs.	Concentration of Cu^{++} (M) × 10	Heat liberated in Joules	Enthalpy change $-\Delta H^\circ$ kJ mol^{-1}	Average $-\Delta H^\circ$ kJ mol^{-1}	$-\Delta G^\circ$ kJ mol^{-1}	ΔS° JK^{-1}
1		68.54	54.48			
2	2.5180	68.80	54.64			
3		68.71	54.56			
4		60.74	54.48			
5	2.2300	60.93	54.64	54.52±0.12	85.90	105.23
6		60.93	54.64			
7		54.27	54.27			
8	2.0000	54.48	54.48			
9		54.56	54.56			

Volume of Cu^{++} soln. taken for reaction = 5 ml.

TABLE 2—ENTHALPY CHANGE FOR $Cu^{++} + 2A^- \rightleftharpoons CuA_2$ IN TERT-BUTANOL-WATER AND GLYCEROL-WATER MEDIA AT 25°C

Wt. % of tert-butanol or glycerol	$-\Delta H^\circ$ kJ mol^{-1} in t-butanol-water	$-\Delta H^\circ$ kJ mol^{-1} in glycerol-water
10	56 65±0.33	59.50±0.08
20	59 12±0.29	62.89±0.08
30	62.80±0.88	61.63±0.17
40	61.34±0.29	60.71±0.21
50	60.17±0.21	59.91±0.17

Discussion

A number of workers have determined the enthalpy of formation of Cu(II)-glycinate in aqueous medium at 25°. The results are given below :

ΔH° kJ mol^{-1}	Method
−54.39	Cal.[4]
−55.15	Cal.[14]
−51.88	Cal.[15]
−53.56*	Cal.[8]
−48.53±2.09	Equil.[11]
−54.52±0.12	Cal. (our value)

(Cal. = calorimetric,

Equil. = temperature dependence of equilibrium constants,

* measured at 20.5°.

Our value is in good agreement with that reported by Gergely and coworkers[4]. Other values differ slightly from our value probably due to the not well-chosen experimental conditions as observed by Gergely *et al*[4].

Figures 1 and 2 represent the plots of $-\Delta H^\circ$ (K cal/mole) against weight percent, mole fraction of organic constituent of the solvent and reciprocal

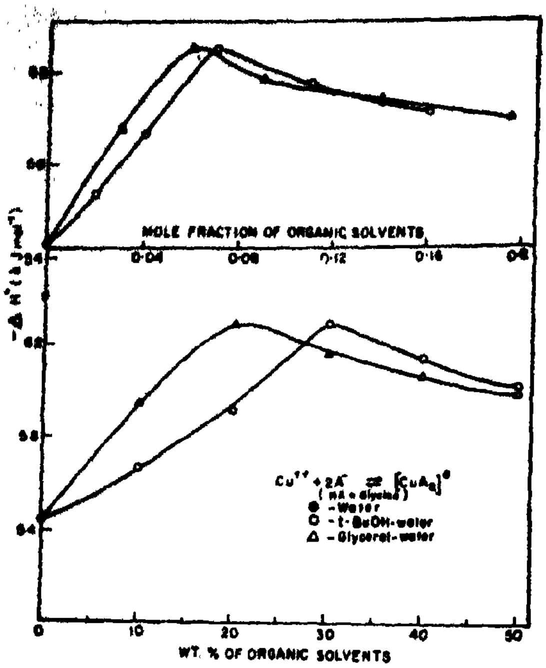


Fig. 1. Plot of -ΔH° against solvent composition.

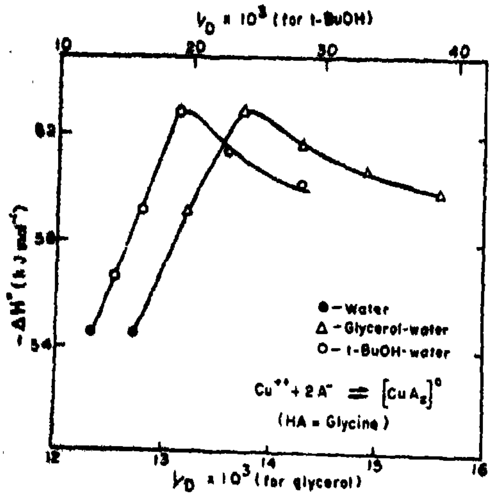


Fig. 2. Plot of $-\Delta H°$ against $\frac{1}{D}$,

of dielectric constant of aqueo-organic solvent. The dielectric constant values necessary are taken from Conway[16] and Akerlof[17].

As may be seen from the diagram, the heat of formation ($-\Delta H°$) passes through a maximum around 30 wt % of tert-butanol in tert-butanol-water system and 20 wt % of glycerol in glycerol-water medium. These findings may be explained in the light of the interpretation of the behaviour of glycine in water and in ethanol-water media by earlier workers[18-21].

Amino acids are highly polar. They contain differing non-polar side chains. Longsworth[18] has studied the diffusion of amino acids in water and has concluded that glycine is a "structure-breaker" in water. Kay and Evans[19] has drawn similar conclusions from the interpretation of the temperature dependence of the walden products of the amino acids in aqueous solution. In addition, Robinson[20] has interpreted the behaviour of the partial molal entropy of water in aqueous solution of the amino acids that glycine is a net "structure-breaker" while the higher aliphatic homologues are "structure makers". Spink and Auker[21] studied the heat of solution of amino acids in water and water-ethanol medium. The positive transfer entropies support the interpretation that glycine is even more effective as a "structure-breaker" in alcohol-water medium than in water, at least up to 0.1 mole fraction of ethanol. The increased "structure-breaking" by glycine in the mixed solvent is likely due to the already enhanced structure in the original solvent mixtures. Thus the unfavourable free-energy of transfer of glycine from water to aqueous ethanol mixtures is a result of "structure-breaking" effect that causes the entropy and enthalpy terms to be positive with the enthalpy contribution dominating. From the present results, glycine appears to be more effective "structure-breaker" in tert-butanol-water and glycerol-water media similar to the observation already reported[21]. The maximum structuration corresponds to maximum enthalpy of transfer.

The maximum structuration of tert-butanol-water mixtures at about 30 wt % also agrees with the observation of Pointud, Morel and Juillard[22], in their study of the behaviour of LiCl in tert-butanol-water medium, both enthalpies and entropies of transfer show maxima at 0.08 mole fraction of tert-butanol (27 wt %).

This maximum structuration model is also supported by some thermodynamic and spectroscopic arguments[23-26].

Acknowledgement

The authors wish to thank the Council of Scientific and Industrial Research, New Delhi for the award of a Research Fellowship to one of them (S. Bandopadhyay).

References

1. Y. Nozaki and C. Tanford, *J. Biol. Chem.*, 1971, **246**, 2211.
2. A. C. R. Thornton and H. A. Skinner, *Trans. Faraday Soc.*, 1969, **65**, 2044.
3. W. F. Stack and H. A. Skinner, *Trans. Faraday Soc.*, 1967, **63**, 1136.
4. A. Gergely, I. Nagypal and I. Sovago, *Acta Chim.*, (Budapest), 1971, **67**, 241.

5. K. P. ANDERSON, D. A. NEWELL and R. M. IZATT, *Inorg. Chem.*, 1966, **5**, 62.

6. M. YOSHINO and M. MAKI, *Nippon Nagaku Zasshi*, 1966, **87**, 796.

7. K. P. ANDERSON, W. O. GREENHALGH and E. A. BUTLER, *Inorg. Chem.*, 1967, **6**, 1056.

8. R. D. GILLARD, H. M. IRVING and L. D. PETTIT, *J. Chem. Soc.* (A), 1968, **4**, 678.

9. G. DEGISCHER and G. H. NANCOLLAS, *J. Chem. Soc.* (A), 1970, **7**, 1125.

10. J. L. MEYER and J. E. BAUMAN, *J. Chem. Engg. Data*, 1970, **15**, 404.

11. V. S. SHARMA and H. B. MATHUR, *Indian J. Chem.*, 1965, **3**, 475.

12. S. BANDYOPADHYAY and S. C. LAHIRI, *J. Indian Chem. Soc.*, 1978, **55**, 1286.

13. S. C. LAHIRI, A. K. ROY and S. ADITYA, *Thermo Chim. Acta.*, 1976, **16**, 277.

14. K. P. ANDERSON, W. O GREENHALGH and R. M. IZATT, *Inorg. Chem.*, 1966, **5**, 2106.

15. R. M. IZATT, J. J. CHRISTENSEN and V. KOTHARI, *Inorg. Chem.*, 1964, **3**, 1565.

16. B. E. CONWAY, Electrochemical Data, Elsevier Publishing Company, Amsterdam Houston, London, 1952.

17. G. AKERLÖF, *J. Amer. Chem. Soc.*, 1932, **54**, 4125.

18. L. G. LONGSWORTH, *J. Amer. Chem. Soc.*, 1953, **75**, 5707.

19. R. L. KAY and D. E. EVANS, *J. Phys. Chem.*, 1966, **70**, 2325.

20. A. L. ROBINSON, *J. Chem. Phys.*, 1946, **14**, 588.

21. C. H. SPINK and M. AUKER, *J. Phys. Chem.*, 1970, **74**, 1742.

22. Y. POINTUD, J. P. MOREL and J. JUILLARD, *J. Phys. Chem.*, 1976, **80**, 2381.

23. E. K. BAUMGARTNER and G. ATKINSON, *J. Phys. Chem.*, 1971, **75**, 2336.

24. F. FRANKS and D. S. REID, Water : Compr. Treatise, 1975, **2**, 356.

25. M. C. R. SYMONS and M. J. BLANDAMER, "Hydrogen Bonded Solvent Systems", Covington and Jones, Ed. Taylor and Francis, London, 1968, p. 211.

J. Indian Chem. Soc.,
Vol LVII, January 1980, pp. 80-85

Use of Cobalt Molybdate in the Catalytic Vapour Phase Oxidation of Toluene

K. P. SRIVASTAVA* and K. L. MADHOK

Department of Chemistry, Birla Institute of Technology and Science, Pilani-333 031 (Raj)

Manuscript received 4 April 1979, revised 23 August 1979, accepted 31 December 1979

The catalytic activity of unsupported and silica, alumina supported Cobalt molybdate was investigated in the vapour phase oxidation of toluene to produce benzaldehyde and benzoic acid. Results on some catalysts which showed an appreciable effect are reported. The temperature, concentration of catalyst and space velocities were varied over a wide range with each catalyst. The best results were obtained with cobalt molybdate, 80% supported on silica gel at a temperature of 500°, space velocity 9730±20 litre hour⁻¹ litre⁻¹, air/hydrocarbon ratio 610. The yield of benzaldehyde on the basis of toluene reacted is 63.23% per pass and conversion to benzaldehyde is 8.51%.

THE oxidation of aromatic compounds for the production of partially oxigenated derivatives has become of great industrial importance. Benzaldehyde finds wide uses in chemical industry. The increasing demand for pure benzaldehyde has stimulated interest in its production by the direct oxidation of toluene vapours in presence of suitable catalysts. Most of the active catalysts systems used to date are covered by patents. In general the catalysts used consist of vanadium and/or molybdenum oxides and a third component, such as TiO_2, CuO and P_2O_5 and they may be either supported or unsupported.

Volynkin[1,2] studied the oxidation of toluene to benzaldehyde over a number of solids, partially reduced catalysts and in presence of catalysts occurring in molten metals. The maximum yield of benzaldehyde reported is 50% (based on the toluene reacted) at 670°, but much higher values have been claimed in the patent literature by Ray *et al*[3]. If V_2O_5, $V_2O_5-MoO_3$ and $MoO_3-P_2O_5$ are used as catalyst, the main oxidation products of toluene are benzaldehyde, benzoic acid with traces of maleic acid CO and CO_2[4,5]. Mamoru and Sadio[6] have reported the enhanced activity of $MoO_3-P_2O_5$ catalyst by the addition of Bi_2O_3.

Recently Sharma and Bhattacharyya[7] have reported the oxidation products of toluene over molten mixed oxides (in fused state).

The present investigation describes our studies on the heterogeneous vapour phase catalytic oxidation of toluene vapours over supported and unsupported cobalt molybdate catalysts.

Experimental

All the chemicals used were either BDH, AnalaR quality or E. Merck 'GR' reagents. Toluene was distilled before it was used.

Catalyst(I), 20% supported cobalt molybdate catalyst was prepared when 22.1 gm sodium molybdate dissolved in hot water was added to known amount of silica gel or alumina gel, containing 80 gm SiO_2 or Al_2O_3 in water and to this 26.58 gm cobalt nitrate dissolved in water was added with constant stirring. The resulting mixture was evaporated on water bath and the solid ($CoMoO_4$/support 1 : 4) was dried. This is finally heated in a furnace at about 550° and sieved to get the −18 +24 Tyler mesh size fraction.

The flow diagram of the apparatus used is shown in Fig. 1. The reactor (R) was made of a pyrex glass tube of internal dia 3 cm and 70 cm long. Another glass tube of 1 cm bore kept concentric with the reactor was used for inserting the thermocouple. Reactor was connected to another glass tube which functions as preheater zone (P.H.). The catalyst was packed in the reactor between two plugs of

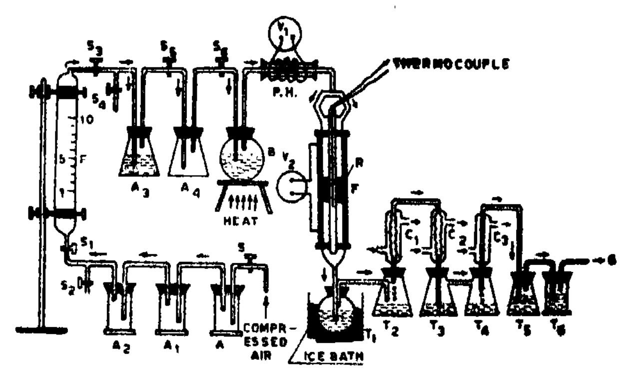


Fig. 1. Apparatus used for the Oxidation of Toluene in a fixed bed.

A, A_1, A_2 Bubblers ; F, Flowmeter ; S_1—S_4, Stop-Cocks ; A_3, Air Dryer ; A_4, Trap ; B ; Toluene Bubbler ; P.H., Preheater ; V_1, V_2 Variable Transformers ; F=Furnace, R, Reactor, T_1—T_4, Product Receiver ; C_1—C_3 Condenser ; T_5, Carbondioxide Trap ; T_6 = Aldehyde Trap ; G. Stack Gases.

purified glass-wool. The reactor and preheater zones were heated by two separate tubular heaters controlled by variable transformers (V_1 & V_2). The temperature of the catalyst bed was measured with a calibrated chromel-alumel thermocouple. After each experiment, the proper packing of the catalyst in the catalyst zone was checked so as to ensure proper gas solid contact during the run.

The catalyst was charged in the reactor. Purified air was bubbled through a toluene bubbler, after passing through a flow meter. Toluene bubbler was heated to 60°, 70° and 100°. The air/toluene mixture thus required was heated to 400° before it was introduced in the reactor.

The reaction products were collected in an air condenser, water condenser and finally through an ice cold condenser. To stop benzaldehyde vapours from escaping along with the air stream the affluent gases were passed through a bubbler containing 2, 4-dinitrophenylhydrazine solution. Carbon dioxide produced in the reaction was absorbed by 250 ml of standard solution of potassium hydroxide (5%), kept in three bubblers. The quantitative estimation of the products was done by the method similar to one suggested by Kumar, Bhat and Kuloor[8]. The specific surface area of the catalyst supports was determined by BET method using nitrogen gas as adsorbent.

Parameters studied :

Runs were carried out with the above catalysts at the following conditions :

(1) Reaction temperature : 350 to 550°

(2) Air-toluene ratio : 350 to 696

(3) Space velocity : 5860 to 14081 ± 1 litre/hr/litre

Definitions :

During the consideration of the results and discussions the various terms used are defined as follows :

(1) Air/Toluene ratio $= \dfrac{\text{Volume of the air in the reaction mixture}}{\text{Volume of the toluene passed}}$

(2) Space Velocity = Volume of the gas mixture (dry air and toluene vapour) at N. T. P. passing per hour per volume of the catalyst litre hr^{-1} $litre^{-1}$.

(3) Conversion % (to a particular product) $= \dfrac{\text{Grams toluene converted to a particular product}}{\text{Grams toluene passed}} \times 100$

(4) Yield of Benzaldehyde. $= \dfrac{\text{Tolune Converted to benzaldehyde}}{\text{Toluene converted to partial and complete oxygenated product}} \times 100$

All temperatures are the temperatures of the catalyst zone.

Results and Discussion

The results obtained with various catalysts are given in Tables 1 to 4, and representative examples have been plotted from these data. The discussion herewith describes the results obtained with catalyst IV, Table 1 ($CoMoO_4$ 80% on SiO_2) in the following manner.

TABLE 1—ACTIVITY DATA FOR VARIOUS CATALYSTS
EFFECT OF TEMPERATURE AT CONSTANT SPACE VELOCITY 9730 ± 20 lit hr^{-1} $litre^{-1}$
APPARENT VOLUME OF THE CATALYST = 30 c.c.

Catalyst	Catalyst composition $CoMoO_4 : SiO_2$	Temperature °C	Air/Toluene ratio	Specific surface area of the catalyst support m^2/gm	Conversion %				Total conversion %	% Yield of BzH
					BzH	BzA	M.A.	CO_2		
I	20 : 80	350	610	86.23	3.87	0.96	0.44	1.91	7.18	53.69
		400	602	88.34	4.98	0.88	1.10	2.14	9.10	54.72
		500	602	98.13	6.28	1.08	1.53	2.01	10.85	57.43
		550	610	97.01	4.90	1.14	1.16	2.17	9.37	52.65
II	40 : 60	350	610	86.23	4.41	0.31	0.48	1.63	6.81	65.16
		400	602	88.34	5.61	1.06	1.37	1.76	9.78	57.79
		500	602	98.13	6.98	1.27	1.82	2.15	12.21	57.79
		550	610	97.01	5.51	1.27	1.41	1.78	9.97	55.86
III	60 : 40	350	602	86.23	4.69	0.89	0.64	1.30	7.52	62.10
		400	602	88.34	4.99	0.98	0.28	1.63	7.88	57.92
		500	610	98.13	7.81	1.38	2.00	1.61	12.80	59.45
		550	602	97.01	6.20	1.46	1.65	1.63	10.94	56.74
IV	80 : 20	350	610	86.23	5.80	1.17	1.15	1.45	9.57	60.58
		400	602	88.34	8.46	1.15	1.15	1.75	12.51	66.35
		500	610	98.13	8.51	1.68	1.75	1.58	13.52	63.23
		550	610	97.01	7.71	1.48	1.83	1.60	12.57	61.71
V	100 : 00	350	602	—	3.15	0.41	0.28	2.11	5.95	53.78
		400	602	—	4.15	0.63	0.93	2.24	7.96	52.91
		500	602	—	5.28	0.81	1.35	2.34	9.78	54.80
		550	602	—	4.09	0.64	1.02	2.24	8.19	50.09

BzH = benzaldehyde ; BzA = benzoic acid ; M.A. = maleic acid.

TABLE 2—ACTIVITY DATA FOR VARIOUS CATALYSTS
EFFECT OF TEMPERATURE AT CONSTANT SPACE VELOCITY, 9730 ± 20 lit hr^{-1} $litre^{-1}$
APPARENT VOLUME OF THE CATALYST = 30 c.c.

Catalyst	Catalyst composition $CoMoO_4$: Al_2O_3	Temperature °C	Air/ Toluene ratio	Specific surface area of the catalyst support m^2/gm	Conversion % BzH	Conversion % BzA	Conversion % M.A.	Conversion % CO_2	Total conversion %	% Yield of BzH
VI	20 : 80	350	602	87.80	2.16	1.00	0.53	3.06	6.75	32.22
		400	610	99.54	3.41	2.05	1.16	3.11	7.73	35.00
		500	610	96.87	3.49	2.22	1.27	3.49	8.47	33.12
		550	610	96.77	2.26	1.41	0.80	3.11	7.58	30.34
VII	40 : 60	350	602	87.80	2.99	1.38	0.77	3.45	8.59	34 80
		400	610	99.54	3.19	1.48	0.89	3.86	9.42	33.90
		500	602	96.87	3.03	1.32	0.78	4.14	9.27	32.70
		550	610	96.77	3.30	1.38	0.84	4.21	9.63	32.84
VIII	60 : 40	350	610	87.80	3.91	1.61	0.77	4.20	10.49	37.25
		400	602	99.54	4.37	1.61	0.92	4.74	11.64	37.63
		500	602	96.87	3.94	1.48	0.90	5.02	11.34	34.81
		550	610	96.77	4.75	1.53	0.92	3.54	10.74	44.19
IX	80 : 20	350	602	87.80	4 01	1.67	0.83	4.45	10.97	36.66
		400	610	99.54	4.37	1.62	0.94	5.60	12.54	34.68
		500	610	96.87	4.32	2.36	1.28	5.60	13.57	31.83
		550	610	96.77	5.12	1.94	1.19	4.81	13.06	39.47
X	100 : 00	350	602	—	3.15	0.41	0.28	2.11	5.95	53.78
		400	602	—	4.15	0.68	0.93	2.24	7.96	52.91
		500	602	—	5.28	0.81	1.36	2.34	9.78	54,30
		550	602	—	4.09	0.84	1.02	2.24	8.19	50,09

BzH = benzaldehyde ; BzA = benzoic acid ; M.A. = maleic acid.

TABLE 3—ACTIVITY DATA FOR VARIOUS CATALYSTS
EFFECT OF SPACE VELOCITY AT CONSTANT TEMPERATURE 500°C, APPARENT VOLUME OF THE CATALYST = 30 c.c.
SPECIFIC SURFACE AREA OF THE CATALYST SUPPORT = 98.13 m^2/gm

Catalyst	Catalyst composition $CoMoO_4$: SiO_2	Space velocity litre $hour^{-1}$ $litre^{-1}$	Air/Toluene ratio	Conversion % BzH	Conversion % BzA	Conversion % M.A.	Conversion % CO_2	Total conversion %	% Yield of BzH
I	20 : 80	5890	350	4.79	0.66	0.94	1.95	8.28	57.34
		9749	602	6.23	1.08	1.53	2.01	10.85	57.43
		14034	696	6.08	0.75	1.09	1.66	9.51	65.05
II	40 : 60	5890	350	5.25	0.59	1.15	1.60	8.89	59.15
		9749	602	6.98	1.27	1.82	2.15	12.21	57.79
		14034	696	6.65	0.91	1.31	1.53	10.47	64.25
III	60 : 40	5860	352	5.51	0.98	1.29	1.47	9.25	59.84
		9711	610	7.31	1.38	2.00	1.61	12.30	59.45
		14034	696	6.96	1.28	1.45	1.37	11.06	63.14
IV	80 : 20	5860	352	6.14	1.31	1.43	1.32	10.20	60.62
		9711	610	8.51	1.68	1.75	1.58	13.52	63.23
		14081	692	5.62	1.35	2.02	1.36	10.69	66.44
V	100 : 00	5890	350	4.03	0.46	0.80	3.03	8.32	56.73
		9749	602	5.28	0.81	1.35	2.34	9.78	54.30
		14034	696	5.23	0.53	0.94	2.04	8.74	65.29

BzH = benzaldehyde ; BzA = benzoic acid ; M.A. = maleic acid.

TABLE 4—ACTIVITY DATA FOR VARIOUS CATALYSTS
EFFECT OF SPACE VELOCITY AT CONSTANT TEMPERATURE 500°C, APPARENT VOLUME OF THE CATALYST=80 c.c.
SPECIFIC SURFACE AREA OF THE CATALYST SUPPORT=96.87 m²/gm

Catalyst	Catalyst composition $CoMoO_4 : Al_2O_3$	Space velocity litre hr^{-1} litre^{-1}	Air/Toluene ratio	Conversion %				Total conversion %	% Yield of BzH
				BzH	BzA	M.A.	CO_2		
VI	20 : 80	5890	350	2.11	1.26	0.72	2.01	6.10	34.92
		9711	610	3.49	2.22	1.27	3.49	8.47	33.12
		14034	630	2.94	2.08	1.00	3.61	9.63	30.23
VII	40 : 60	5890	350	3.70	1.60	0.96	3.47	9.73	38.16
		9749	602	3.08	1.32	0.74	4.14	9.27	32.70
		14081	692	3.01	1.26	0.77	4.16	9.22	32.69
VIII	60 : 40	5890	350	4.85	1.85	0.90	4.32	11.98	40.52
		9749	602	3.94	1.48	0.90	5.02	11.34	34.81
		14081	692	4.00	1.80	0.80	3.27	10.07	39.76
IX	80 : 20	5890	350	5.26	1.89	1.02	4.81	12.99	40.76
		9711	610	4.32	2.36	1.28	5.60	13.57	31.83
		14081	692	4.27	0.18	1.09	4.44	9.99	37.62
X	100 : 00	5890	350	4.03	0.46	0.80	3.03	8.32	56.78
		9749	602	5.28	0.81	1.35	2.34	9.78	54.80
		14034	696	5.23	0.53	0.94	2.04	8.74	65.29

BzH = benzaldehyde ; BzA = benzoic acid ; M.A. = maleic acid.

Effect of Cobalt Molybdate Concentration :

It is seen from the Fig. 2 that the activity of cobalt molybdate, unsupported, varied with change in its concentration supported on silica gel. The data show that under almost identical conditions maximum conversion of 8.51% yield 63.23% of benzaldehyde was obtained when the ratio of cobalt molybdate silica was 80 : 20, while with the catalyst supported on alumina the maximum conversion to benzaldehyde is 5.26%, Table 3. Probably this composition corresponds to maximum electron work function of the system studied. Margolis *et al.*[9] reported that for the oxidation of propene to acrolein by bismuth oxide-molybdenum oxide catalysts the electron work function and activity passes through a maximum with increasing atomic percentage of bismuth in the $Bi_2O_3.MoO_3$ system.

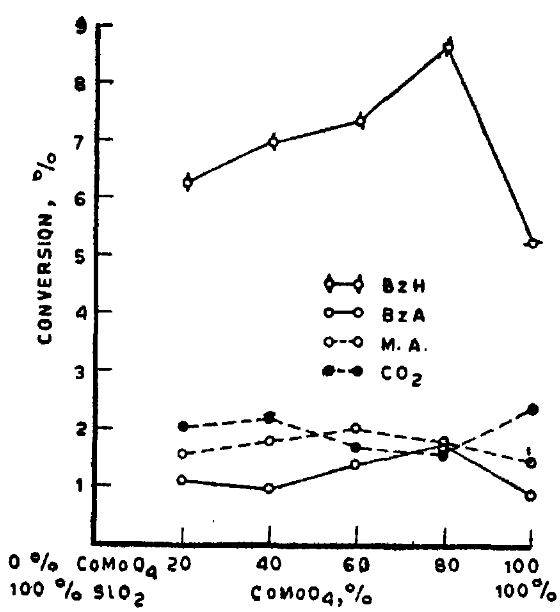


Fig. 2. Effect of catalyst composition ($CoMoO_4 : SiO_2$ ratio) on the conversion per cent. Space velocity, 9711—9749 litre hr^{-1} litre^{-1}, temperature 500°±5, Air Toluene ratio, 602—610.

Effect of Temperature :

The influence of temperature on the conversion is shown in Fig. 3. The optimum temperature obtained in the reaction was 500°. A rise in temperature beyond the optimum value favoured the formation of carbon dioxide and the yield of the

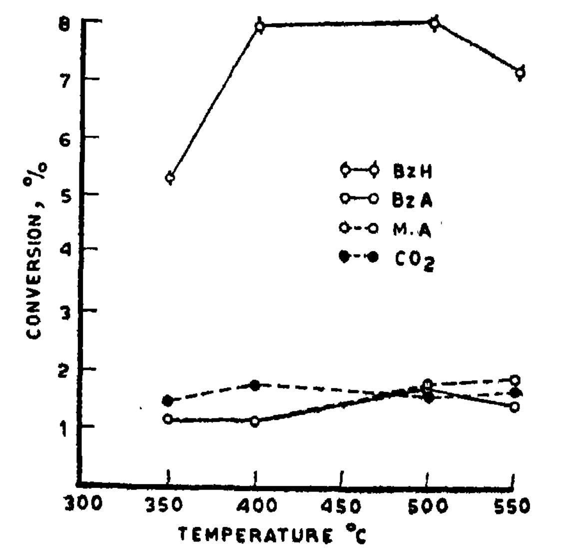


Fig. 3. Effect of temperature on the conversion to various products with catalyst IV ($CoMoO_4$ 80% on SiO_2). Space velocity 9730±20 litre hr^{-1} litre^{-1}, Air/Toluene ratio 605±5.

benzaldehyde declined considerably. The efficiency and activity of the catalyst IV was found to be quite sensitive to temperature.

Effect of Space Velocity :

The effect of space velocity on the selectivity and hence activity of the catalyst IV is shown in Fig. 4. The value of space velocity 9711 litre hour^{-1} litre^{-1} was found to be optimum. Any increase in space velocity beyond the optimum value lowered the yield of the benzaldehyde. The lowering of per cent conversion and hence yield of the benzaldehyde with increasing space velocity beyond the optimum may be due to the considerable decrease in the contact time.

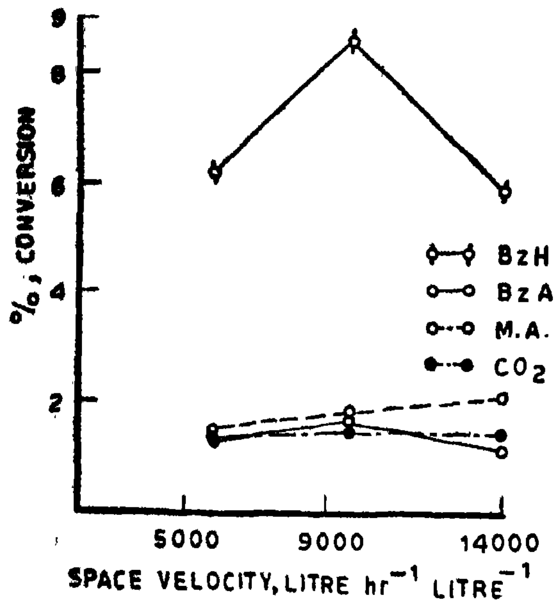


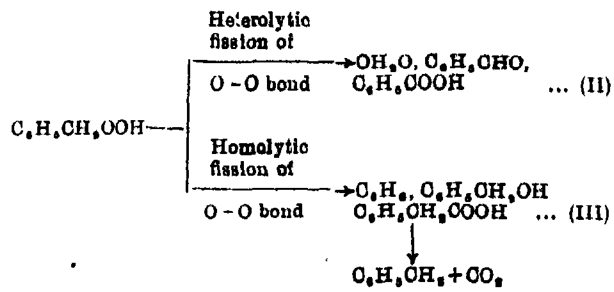
Fig. 4. Effect of space velocity on the conversion to various products in the presence of catalyst IV ($CoMoO_4$: 80% on SiO_2), temperature 500±5°, Air/Toluene 650±40.

The main products of toluene oxidation are benzaldehyde, benzoic acid, maleic acid and carbon dioxide. Bone[10] has reported the formation of benzyl alcohol in the oxidation of toluene, but as such it has not yet been isolated. The possibility for the absence of benzyl alcohol in the products of toluene oxidation is that it might have been consumed by some reactions with toluene which went much faster than its total oxidation or its partial oxidation to benzaldehyde. Some reliable evidence regarding this possibility is available in the homogeneous gas phase oxidation of toluene[11].

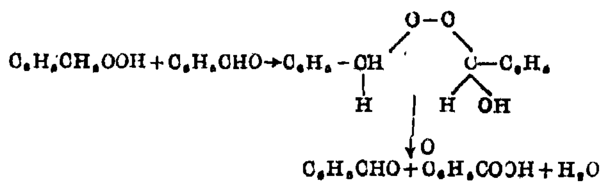
The reaction initiated through a hydroperoxide[12] which is probably the first intermediate formed in the oxidation of toluene, seems to be more feasible particularly in the presence of active catalyst and is given below

$$C_6H_5CH_3 + O_2 \longrightarrow C_6H_5CH_2OOH \quad \dots (1)$$

This intermediate is not very stable because of the availability of orthoelectron to hydroperoxidyl OH and according to suggested mechanism[13], (1), peroxy compounds can decompose in two fashions, one of which leads to the formation of alcohol.



In the presence of benzaldehyde, the possibility of $C_6H_5CH_2OOH$ radical to undergo reaction II would be high



In the present case also we could not isolate the benzyl alcohol hence the probable reaction may follow the path II as suggested.

Parks and Katz[14] have studied the heterogeneous vapour phase oxidation of toluene and found the exothermic nature of the reaction. The maximum increase in the catalyst temperature was recorded to be 50°. In our present case we have observed that the heat generated during the reaction would not be enough to raise the temperature of the catalyst bed by more than 20°.

Acknowledgement

The authors are thankful to the authorities of Birla Institute of Technology and Science, Pilani for providing necessary facilities and to the University Grants Commission, New Delhi for the award of a fellowship to one of them (KLM). The helpful discussions by Shri I.K. Jain are greatly acknowledged.

References

1. N. I. Volynkin, *Zh. Prikl. Khim., Leningr.*, 1971, **44**(8) 1858.

2. N. I. Volynkin, *Zh. Prikl. Khim., Leningr.*, 1968, **41**(6), 1376.
3. S. K. Ray, G. N. Kulshrestha, G. S. Murty, H. S. Rao and A. Lahiri, *Chem. Abs.*, 1970, **72**, 48155.
4. A. I. Mamoru, *Kogyo Kagaku Zasshi*, 1970, **73**(5), 946.
5. A. I. Mamoru, *Kogyo Kagaku Zasshi*, 1971, **74**(8), 1636.
6. A. I. Mamoru and S. J. Sadio, *J. Chem. Soc.*, Japan, 1972, **6**, 1151.
7. V. K. Sharma and S. K. Bhattacharyya, *Indian Jour. of Technol.*, 1976, **14**, 488.
8. R. N. Kumar, G. N. Bhat and N. R Kuloor, *Curr. Sci.*, 1962, **31**, 491.
9. L. Ya. Margolis, *Advances in Catalysis*, 1963, **14**, 429.
10. Bone, *J. Soc. Chem. Ind.*, 1934, **53**, 963.
11. C. F. Cullis and A. Fish, *The Chemistry of Carbonyl Groups.*, 1966, 120.
12. S. K. Bhattacharyya and V. K. Sharma, *Indian Jour. of Technol.*, 1976, **14**, 492.
13. Gould and S. Edvin, Mechanism and Structure in Organic Chemistry, 1959, 711.
14. W. G. Parks and J. Katz, *Ind. Eng. Chem.*, 1936, **28** 319.

J. Indian Chem. Soc.,
Vol. LVII, January 1980, pp. 86-88

Synthesis of Some Trifluromethylphenazines

K. D. BANERJI, A. K. D. MAZUMDAR, N. K. SAHA and S. K. GUHA

Chemical Laboratory, Marwari College, Bhagalpur University, Bhagalpur-812 007

Manuscript received 27 April 1979, revised 20 November 1979, accepted 23 November 1979

Synthesis and properties of several trifluromethylphenazines containing the acenaphthene, isatin and phenanthrene nuclei have been reported.

ACENAPHTHAPHENAZINES, indophenazines and phenanthraphenazines have been studied principally as dyes[1-10], Isatin and its derivatives have been found to be associated with antiviral[11], antibacterial[12], anthelminitic[13] and hypotensive[14] activity. Again biological activity of indophenazines[15-19] and their use as optical bleaches[20] has also received attention, whereas phenanthraphenazines have been found to possess both anticancer and cancer inducing properties[21,22].

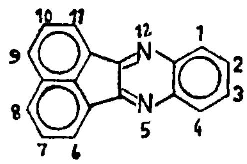
Study of halogen containing phenazines is meagre[23] and no study appears to have been directed to phenazines containing fluorine atom, although a variety of fluorine containing compounds have been observed to show significant biological activity[24-28]. A series of investigations on fluorine containing phenazines have, therefore, been presently undertaken in our laboratory (partly reported)[29]. In this communication we report about acenaphthaphenazines(I), indophenazines(II) and phenanthraphenazines(III) all of which contain three fluorine atoms forming a trifluoromethyl group attached to the benzenoid ring at position 2 or 3.

These phenazines have been prepared by the condensation of 4-trifluoromethyl-*o*-phenylenediamine[30], with

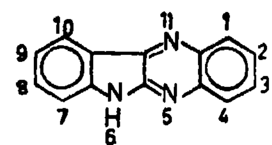
(a) acenaphthenequinone and its 3-chloro-, 3-bromo- and 3 : 4-dinitro-derivatives to yield compounds of type I.

(b) isatin and its 5-bromo-, 5-chloro, 5-nitro, 5-iodo-, 5 : 7-dibromo- and 5-bromo-7-nitro-derivatives to produce phenazines of the type II and

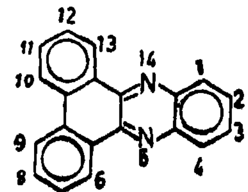
(c) phenanthraquinone and its 2-nitro-and 2 : 7 dinitro-derivatives to give compounds of the type III.



I



II



III

These condensations in general occur smoothly. The acenaphthaphenazines and phenanthraphenazines are yellow whereas the indophenazines are yellow to deep yellow (with the exception of Sl. No. 5 which forms greenish silky needles from ethyl acetate). Theoretical possibility of the production of structural isomer exists in a few cases, but it was observed that one isomer was predominantly produced which could be obtained in a pure state.

The phenazines reported here could not be developed well on wool and do not appear to be of much value as dyestuffs. All the above phenazines are soluble in methanol, ethanol, ethyl acetate, chloroform, benzene, pyridine and nitrobenzene. Details about the colour, yield, solvent of crystallisation are given in the Table. Biological assay of a few selected compound is proposed to be undertaken.

Experimental

The diketone was first dissolved in minimum volume of boiling glacial acetic acid and then molar proportion of 4-trifluoromethyl-*o*-phenylenediamine was added, and refluxing was continued. The resulting phenazines were thrown out of the solution immediately in most cases but the mixture was kept

TABLE 1—ISATIN = I ; ACENAPHTHENEQUINONE = AQ ; PHENATHRAQUINONE = PQ ; INDOPHENAZINES = IP ; ACENAPHTHAPHENAZINE = AP ; PHENANTHRAPHENAZINES = PP ; 4-TRIFLUOROMETHYL-*o*-PHENYLENEDIAMINE = TOP

Sl. No.	Reactants	Name of the Product	Apperence solvent	M.P. °C %yield of crude	Molecular formula	Colouration with conc. H_2SO_4	Analysis of Nitrogen Required	Found
1	2	3	4	5	6	7	8	9
1.	AQ+TOP	2-Trifluoromethyl AP	Light yellow Pyridine	280-81 90	$C_{19}H_9F_3N_2$	Brownish yellow	8.69	8.81
2.	3-Chloro-AQ+TOP	2-Trifluoromethyl-8-(or- 9) Chloro AP	Light Brown Ethylacetate	179-80 98	$C_{19}H_8ClF_3N_2$	Red	7.85	8.12
3.	3-Bromo-AQ+TOP	2-Trifluoromethyl-8-(or- 9) bromo AP	Light yellow Ethylacetate	174-75 81	$C_{19}H_8BrF_3N_2$	Bright red	6.98	7.14
4.	3 : 4-Dinitro-AQ+TOP	2-Trifluoromethyl-8 : 9-dinitro AP	Brownish yellow Ethylacetate	243-44 100	$C_{19}H_7F_3N_4O_4$	Yellow	7.29	7.41
5.	I+TOP	2-(or -3)Trifluoromethyl IP	Parrot green Ethylacetate	294-95 65	$C_{15}H_8N_3F_3$	Reddish-brown	14.63	15.11
6.	5-Chloro-I+TOP	2-(or- 3) Trifluoro-methyl-9-chloro IP	Yellow needles Methanol	272 73 62	$C_{15}H_7ClF_3N_3$	Deep-brown	13.02	13.25
7.	5-Bromo-I+TOP	2-(or -3) Trifluoro-methyl-9-bromo IP	Yellow needles Methanol	281-82 80	$C_{15}H_7BrF_3N_3$	Deep-brown	11.48	11.51
8.	5-Iodo-I+TOP	2-(or -3) Trifluoro-methyl-9-iodo IP	Brownish yellow Ethylacetate	316-17 48	$C_{15}H_7F_3IN_3$	Deep-brown	10.169	10.24
9.	5-Nitro-I+TOP	2-(or -3) Trifluoro-methyl-9-nitro IP	Deep-orange Pyridine	329-30 95	$C_{15}H_7F_3N_4O_2$	Deep-orange	16.86	17.12
10.	5:7-Dibromo-I+TOP	2-(or -3) Trifluoro-methyl 7 : 9-dibromo IP	Orange Acetic acid	296-97 72	$C_{15}H_6Br_2F_3N_3$	Yellow	9.44	9.58
11.	5-Bromo-7-Nitro-I+TOP	2-(or -3) Trifluoro-methyl-7-nitro-9-Bromo IP	Orange Acetic acid	278-79 100	$C_{15}H_6BrF_3N_4O_2$	Orange	13.63	13.82
12	PQ+TOP	2-Trifluoromethyl PP	Dull green Ethylacetate	184-85 88	$C_{21}H_{11}F_3N_2$	Scarlet red (Bright)	8.045	8.18
13.	2-Nitro-PQ+TOP	2-Trifluoromethyl-7-(or -12)-nitro PP	Deep yellow Pyridine	272-73 43	$C_{21}H_{10}F_3N_3O_2$	Chocolate-brown	10.69	10.81
14.	2: 7-Dinitro-PQ+TOP	2-Trifluoromethyl-7 : 12-dinitro PP	Pale-yellow Pyridine	320-21 88	$C_{21}H_9F_3N_4O_4$	Orange	12.79	13.11

boiling for 5-10 mins, to ensure complete reaction. After cooling, the solids were removed by filtration, washed and crystallised from appropriate solvent.

Acknowledgement

The authors thank the authorities of the Bhagalpur University and Principal, Marwari College, Bhagalpur, for facilities.

References

1. D. PRASAD, S. SEN and P. C. DUTTA, *Ber.*, 1937, **70**(II), 2363.
2. A. C. SARKAR and S. K. GUHA, *J. Chem. Soc.*, 1924, **125**, 335.
3. S. K. GUHA, *J. Chem. Soc.*, 1931, 582.
4. S. K. GUHA, *J. Indian Chem. Soc.*, 1932, **9**, 423.
5. S. K. GUHA, K. D. BANERJI and K. K. SEN, *J. Indian Chem. Soc.*, 1971, **48**, 1011.
6. E. SEHUNEK and L. MARCHLEWSKI, *Ber.*, 1956, **29**, 194.
7. S. K. GUHA, *J. Indian Chem. Soc.*, 1956, **13**, 571.
8. H. D. TIWARI and S. D. DUTTA, *Proc. Nat. Acad. Sci.*, (Allahabad), 1937, **71**, 58.
9. S. K. GUHA, K. D. BANERJI and K. K. SEN, *J. Indian Chem. Soc.*, 1973, **50**, 264.
10. S. K. GUHA, K. D. BANERJI and K. K. SEN, *J. Indian Chem. Soc.*, 1972, **49**, 815.
11. T. S. OSDANE in Medicinal Chemistry, 3rd Ed., A. BURGER, Editor (Wiley Interscience, New York), 1970, p. 662.
12. R. S. VERMA and W. L. NOBLES, *J. Pharma. Sci.*, 1975, **64**, 881
13. R. CAVIER, R. ROVER, R. RIPS and L. RENE, *Chim. Ther.*, 1969, **4**, 21 ; *Chem., Abs.*, 1969, **70**, 113686.
14. JOHN WYETH and Brothers Ltd., Brit., 1,240,648 (1971) ; *Chem. Abs.*, 1971, **75**, 118842.
15. N. P. BUU-HOI, R. ROYER, B. EKKART and P. JACQUIGNON, *J. Chem. Soc.*, 1952, 4867.
16. V. Q. YEN, N. P. BUU-HOI and N. D. XUONG, *J. Chem. Soc.*, 1958, **23**, 1858.
17. N. P. BUU-HOI and P. JACQUIGNON, *J. Chem. Soc.*, 1959, 3095.
18. N. P. BUU-HOI and G. SAINT-RUF, *Bull. Soc. Chem*, France, 1960, 1920 ; *Chem. Abs.*, 1962, **57**, 882.
19. N. P. BUU-HOI, G. SAINT-RUF, P. JACQUIGNON and M. MARTY, *J. Chem. Soc.*, 1963, 2274.
20. J. S. FRIEDMAN U. S. PATENT 2, 627, 461 (1953) ; *Chem. Abs.*, 1958, **47**, 882.
21. D. PRASAD and P. C. DUTTA, *Ber.*, 1937, **70B**, 2365.
22. GEORGES RUDALI, HUGUELET CHALEVET and FRANCIS WINTERNITZ, *Compt. Rend.*, 1955, **240**, 1738.
23. A. R. KATRITZKY in "Advances in Heterocyclic Chemistry", Academic Press, New York and London, 1974, Vol. 18, p. 87.

24. A. Sveinbjornsson and C. A. Vander Werf, *J. Amer. Chem. Soc.*, 1951, **73**, 869.

25. F. C. Schmelkes and M. Rubin, *J. Amer. Chem. Soc.*, 1944, **66**, 1631.

26. H. K. Mitchell and C. Niemann, *J. Amer. Chem. Soc.*, 1947, **67**, 1232 ; E. L. Bannet and C. Niemann, *J. Amer. Chem. Soc.*, 1950, **72**, 1800.

27. R. Duschinsky and E. Pleven, *J. Amer. Chem. Soc.*, 1957, **79**, 4559.

28. W. T. Smith (Jr.) and E. C. Steinle (Jr.), *J. Amer. Chem. Soc.*, 1953, **75**, 1292.

29. K. D. Banerji, A. K. D. Mazumdar, K. Kumar and S. K. Guha, *J. Indian Chem. Soc.*, 1979, **56**, 396.

30. Very recently made commercially available by M/s Maybridge Chemical Company Ltd., U. K.

J. Indian Chem. Soc.,
Vol. LVII, January 1980, pp. 89-91

Synthesis of Unsymmetric *Bis*-Coumarinoxy-Alkanes

K. A. THAKAR*, (MRS.) R. V. PATHAK and (MISS) ACHLA B. DUMIR

Chemistry Department, Marathwada University, Aurangabad-431 004

Manuscript received 8 January 1979, revised 11 July 1979, accepted 23 November 1979

Several unsymmetric *bis*-coumarinoxy alkanes have been synthesised by the condensation of α-coumarinoxy-ω-bromo alkanes with variously substituted hydroxy coumarins in the presence of acetone and potassium carbonate.

COUMARINS are known to possess antifungal and antibacterial properties[1-3]. Disodium cromoglycate (DSCG) which was prepared by Cairns *et al*[4] is known to possess antiasthmatic properties. Some symmetric *bis*-coumarinoxy alkanes which were prepared by us[5] are found to possess antiallergic activity[6]. Taking into account the general activities of coumarins, DSCG and sym. *bis*-coumarinoxy alkanes it was thought that the unsym. *bis*-coumarinoxy alkanes may possess interesting physiological activity. With this in view the synthesis of unsym. *bis*-coumarinoxy alkanes was carried out.

We have synthesised several unsym. *bis*-coumarinoxy alkanes taking into account the parameters like (i) substituents in the benzenoid part, (ii) substituents in the α-pyrone ring, (iii) the length of the alkane chain and (iv) the position of the attachment of ether linkage to benzene ring.

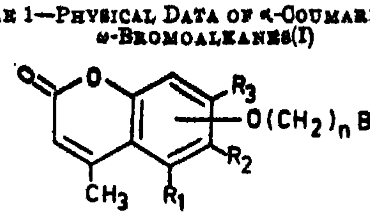
Hydroxy coumarins, the starting materials for the preparation of unsym. *bis*-coumarinoxy alkanes, were prepared by the known methods[7]. One mole of hydroxy coumarin when refluxed with one mole of dihaloalkane in the presence of potassium carbonate and dry acetone gave a mixture of α-coumarinoxy-ω-bromoalkane(I) and sym. *bis*-coumarinoxy alkane[8]. These compounds were separated by extraction with ether, since α-coumarinoxy-ω-bromoalkane is soluble in ether and *bis*-coumarinoxy alkane is insoluble in ether. The physical data of α-coumarinoxy-ω-bromoalkanes used in this work is given in Table 1.

These α-coumarinoxy-ω-bromoalkanes were condensed with variously substituted hydroxy coumarins to get unsym. *bis*-coumarinoxy alkanes (II-VII). The physical data of these compounds is represented in Table 2.

Infrared: IR spectra (Nujol) of unsymmetric compounds showed bands around 1720, 1630 and 1270 cm^{-1} characteristic of C=O of coumarins, C=C and asymmetric stretch of ether linkage respectively.

* Address for correspondence.

TABLE 1—PHYSICAL DATA OF α-COUMARINOXY-ω-BROMOALKANES(I)



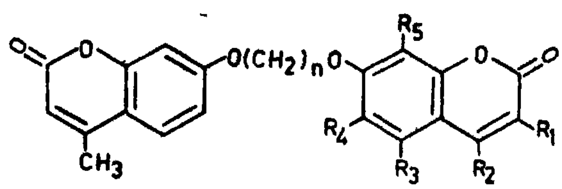
I

Sl. No.	R_1	R_2	R_3	n	Linkage	M.P.°C
1.	H	H	—	2	7′	112-13[b]
2.	H	H	—	3	7′	83[b]
3.	H	H	—	4	7′	66[a]
4.	H	H	—	5	7′	60[c]
5.	H	—	H	2	6′	109[a]
6.	H	—	H	3	6′	85-86[b]
7.	—	H	CH_3	4	5′	119-20[b]

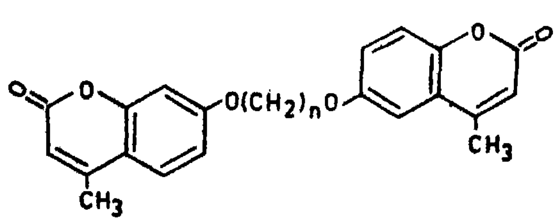
All compounds were obtained in 30-40% yield and gave satisfactory C and H analyses.

a=crystallised from methanol,
b=crystallised from ethanol,
c=crystallised from petroleum ether.

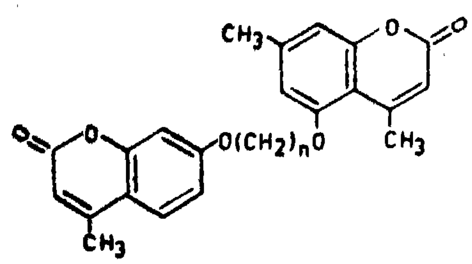
TABLE 2—PHYSICAL DATA OF UNSYMMETRIC *Bis*-COUMARINOXY ALKANES (II-VII)



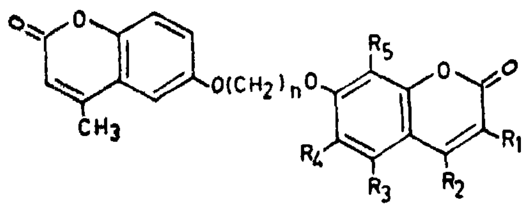
II



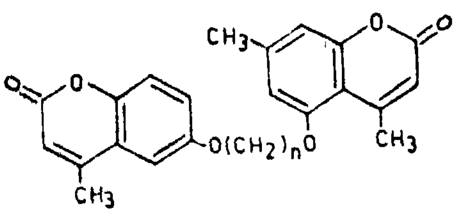
III



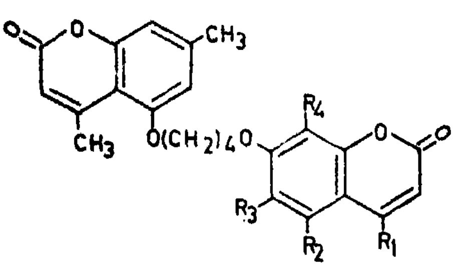
IV



V



VI



VII

(Table 2 Contd.)

Sl. No.	R_1	R_2	R_3	R_4	R_5	n	M.P. °C
			Compound II				
1.	H	CH_3	H	C_2H_5	H	2	223[b]
2.	H	CH_3	H	H	CH_3	2	240[a]
3.	Cl	CH_3	H	H	H	2	241-42[a]
4.	H	H	CH_3	H	H	2	231[a]
5.	H	CH_2COOCH_3	H	H	H	2	193-95[a]
6.	H	CH_3	H	C_2H_5	H	3	175-76[b]
7.	H	CH_3	H	H	CH_3	3	223-24[a]
8.	Cl	CH_3	H	H	H	3	220[a]
9.	H	H	CH_3	H	H	3	168-69[b]
10.	H	CH_2COOCH_3	H	H	H	3	192-93[a]
11.	H	CH_3	H	C_2H_5	H	4	160-61[b]
12.	H	CH_3	H	H	CH_3	4	197-99[a]
13.	Cl	CH_3	H	H	H	4	155[b]
14.	H	H	CH_3	H	H	4	180[b]
15.	H	CH_3	H	H	CH_3	5	146-47[b]
16.	Cl	CH_3	H	H	H	5	164-65[a]
			Compound III				
17.	—	—	—	—	—	2	214-15[a]
18.	—	—	—	—	—	3	190[b]
19.	—	—	—	—	—	4	122-23[c]
20.	—	—	—	—	—	5	168-70[a]
			Compound IV				
21.	—	—	—	—	—	2	252-53[a]
22.	—	—	—	—	—	3	194-95[a]
23.	—	—	—	—	—	4	223-24[a]
24.	—	—	—	—	—	5	195[a]
			Compound V				
25.	H	CH_3	H	C_2H_5	H	2	167-68[b]
26.	H	CH_3	H	H	CH_3	2	225-26[a]
27.	Cl	CH_3	H	H	H	2	227[a]
28.	H	H	CH_3	H	H	2	210[a]
29.	H	CH_2COOCH_3	H	H	H	2	183-84[b]
30.	H	CH_3	H	C_2H_5	H	3	197-98[a]
31.	H	CH_3	H	H	CH_3	3	194-95[b]
32.	Cl	CH_3	H	H	H	3	214-15[a]
33.	H	H	CH_3	H	H	3	192-93[a]
34.	H	CH_2COOCH_3	H	H	H	3	165-66[b]
			Compound VI				
35.	—	—	—	—	—	2	220[a]
36.	—	—	—	—	—	3	238-3[illegible][a]
			Compound VII				
37.	CH_3	H	H	CH_3	—	4	241-42[a]
38.	CH_3	H	C_2H_5	H	—	4	215[a]
39.	H	CH_3	H	H	—	4	175[b]

All compounds gave satisfactory C and H analyses.

a = crystallised from acetic acid,
b = crystallised from 80% acetic acid,
c = crystallised from 60% acetic acid.

Experimental

General procedure for the preparation of—

(i) α-Coumarinoxy-ω-bromoalkanes : A mixture of hydroxy coumarin (0.1 mole), dibromoalkane (0.1 mole), anhydrous potassium carbonate (0.2 mole) and dry acetone was refluxed for 8-10 hrs. Acetone was distilled off and residue was poured over ice water. The solid obtained after filtration was washed with a dilute solution of sodium hydroxide and extracted with ether. α-Coumarinoxy-ω-bromoalkane was obtained by the evaporation of ether. Yield : 30-40%.

(ii) Unsymmetric bis-coumarinoxy alkanes : α-Coumarinoxy-ω-bromoalkane (0.01 mole) was refluxed with hydroxy coumarin (0.01 mole) in the presence of anhydrous K_2CO_3 (0.02 mole) and acetone for 13-14 hrs. The solid obtained after the distillation of acetone was poured over ice and water. The solid obtained after the filtration was washed with a dilute solution of sodium hydroxide. This solid was finally washed with ether to remove excess α-coumarinoxy-ω-bromoalkane. The products were crystallised from the proper solvents. Yield : 70-80%.

Acknowledgement

Author (A.B.D.) is thankful to CSIR, New Delhi, for the award of Post-doctorate Fellowship and author (R.V.P.) to U.G.C. for the award of Junior Research Fellowship.

References

1. K. Okumara, K. Asin and T. Okuda, *Yakugaku Zasshi*, 1961, **81**, 1482.
2. A. Del Campo and P. L. Fazzi, *Riv. Ist. Sieroterap Ital*, 1958, **33**, 389.
3. S. S. Kumari, K. S. R. M. Rao and N. V. S. Rao, *Proc. Indian Acad. Sci.*, 1973, **77**, 149.
4. H. Cairns, C. Fitzmaurice, D. Hunter, P. B. Johnson, J. King, T. B. Lee, G. H. Lord, R. Minshull and J. S. G. Cox, *J. Medni Chem.*, 1972, **15**, 583.
5. K. A. Thakar and A. B. Dumir, *Indian J. Chem.*, 1977, **15B**, 1050.
6. K. A. Thakar and A. B. Dumir, *Indian J. Exptl. Biology*, 1978, **16**, 732.
7. S. Sethna and R. Phadke, *Organic Reactions*, Vol. VII, edited by R. Adams (John Wiley, London), 1953, p. 1.
8. K. A. Thakar and A. B. Dumir, *Indian J. Chem.*, 1977, **15B**, 1054.

NOTES

Studies on Dioxomolybdenum(VI) Complexes of some N – O Donors

S. N. PODDAR, S. GHOSH* and G. C. SAMANTA

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-700 032

Manuscript received 8 August 1979, accepted 30 November 1979

CHEMISTRY of molybdenum(VI) has assumed immense importance because of its presence in certain metalloenzymes and also because of its capacity to effect nitrogen fixation when present in appropriate donor surroundings[1-4]. In the present study we report the syntheses and characterization of several complexes MoO_2^{+2} species in mixed N – O donor surroundings and incorporating Cl^- in the first co-ordination sphere. Some of these complexes possess the general characteristics of a molybdenum complex capable of fixing nitrogen.

A number of molybdenum(VI) complexes containing the MoO_2^{+2} cation of some aromatic acid-hydrazides have been synthesized and characterized. Complexes of dioxomolybdenum(VI), with the Schiff bases derived from the aromatic acidhydrazides as the amine components and diacetylmonoxime and salicylaldehyde as the carbonyl components, have also been prepared and characterized by elemental analysis, uv-visible, and IR spectral study, magnetic susceptibility measurement and measurement of conductance in solution. Though, the oxomolybdenum source used in all the preparations was $(NH_4)_2[MoOCl_5]$ containing the MoO^{+3} species, all the isolated compounds contain the MoO_2^{+2}-cation containing Mo(VI), due to oxidation of the MoO^{+3} moiety by atmospheric air. Most of the compounds contain coordinated chloride ions.

Experimental

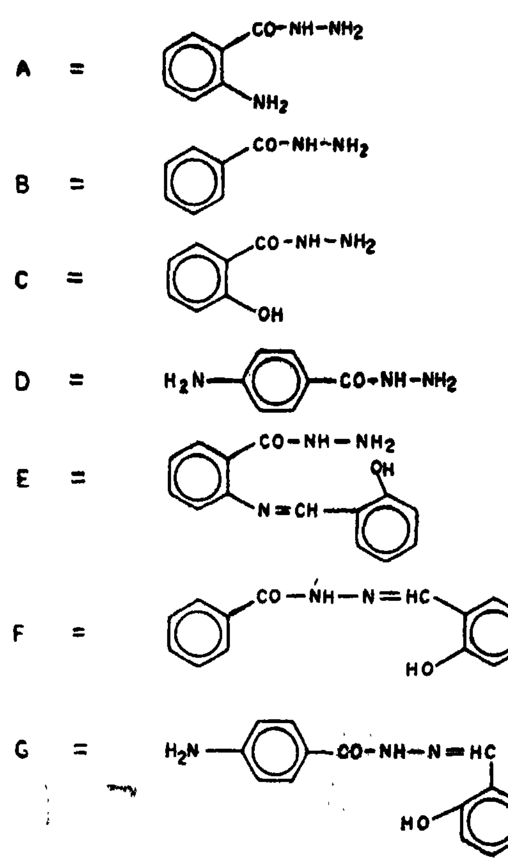
Ammonium oxopentachloromolybdate was prepared by standard method[5].

The complexes were prepared by the following general method.

The ligands (0.002 mole) were taken in alcoholic solution by refluxing and ammonium oxopentachloro molybdate (0.001 mole) added directly to the solution, refluxed for 1½-2 hours and cooled. The solid complexes formed were filtered, washed with alcohol and dried over fused $CaCl_2$.

All the chemicals used were of A.R. B.D.H. grade or of equivalent quality.

The ligands are depicted as follows



$A,B,C,D = LH$ and $E,F,G = L'H_2$

The analytical results of the complexes along with the magnetic moment and electronic spectra, were reported in Table 1. Electronic spectra in solution were recorded in a Hilger UVISPEK spectrophotometer, while the IR spectra were obtained in KBr-matrix in a Beckman IR 20A spectrometer with CsBr optics. Mull spectra in nujol were taken in a spectro MOM 201 (Hungarian) spectrophotometer. Magnetic susceptibility measurements were made in a Guoy balance using $CoHg(SCN)_4$ as the calibrant.

* To whom all correspondences are to be addressed.

TABLE 1

Ligand	Compound	%of Metal found	%of Nitrogen found	%of Halide found	M. P. °C	Colour	Mol. wt.	Absorption spectra λ_{max}
A	$MoO_2(C_7H_9N_3O)Cl_2$ (I)	27.61 (27.42)	11.90 (12.00)	20.10 (20.28)	210	Orange yellow	350	335 in methanol
B	$MoO_2(C_7H_8N_2O)Cl_2$ (II)	29.20 (28.65)	8.48 (8.35)	21.12 (21.19)	250	Orange yellow	335	305 in mull
C	$MoO_2(C_7H_7N_2O_2)Cl$ (III)	29.97 (30.62)	8.82 (8.98)	11.45 (11.32)	250	Buff coloured	318.5	315 in mull
D	$MoO_2(C_7H_9N_3O)Cl_2$ (IV)	27.19 (27.42)	11.85 (12.00)	20.14 (20.28)	235	Orange yellow	350	290 in methanol
E	$MoO_2(C_{14}H_{12}N_3O_2)Cl$ (V)	22.80 (22.93)	10.12 (10.03)	8.60 (8.48)	235	Brown	418.5	325 in mull
F	$MoO_2(C_{14}H_{10}N_2O_2)Cl$ (VI)	24.18 (23.79)	6.85 (6.94)	8.85 (8.79)	270	Brown	403.5	300 in methanol
G	$MoO_2(C_{14}H_{12}N_3O_2)Cl$ (VII)	23.24 (22.93)	10.15 (10.03)	8.42 (8.48)	Above 300	Brownish Black	418.5	285 in 385 methanol

The figures in the parentheses indicate the calculated values.

Discussions

MoO_2^{+2} complexes of the acid hydrazides :

All the complexes isolated possess the general formula MoO_2LHCl_2, where LH is a hydrazide molecule acting in the keto form. All the complexes are diamagnetic in nature, indicating the presence of Mo(VI) species. The strong IR bands in the region 945-975 cm^{-1} give evidence of the presence the MoO_2^{+2} [6] in all the complexes. The lowering of the ν>C=O band of the acidhydrazides on complex formation, points to co-ordination through the carbonyl oxygen. The shift of the N–H stretching mode towards lower frequency in the complexes indicates co-ordination from the terminal $-NH_2$ of the hydrazide moiety[7]. All the hydrazides co-ordinate in the keto form, which is concluded from the presence of two Cl^- ions per MoO_2^{+2} species, as well as from the absence of a very strong band around 1590-1600 cm^{-1} due to the ν>C=N band, which would have appeared, if the ligands were present in the enol form.

Complexes II-IV (Table 1) react with heterocyclic bases like pyridine and picolines to yield species of the general nature $[MoO_2(L)(B)_2]Cl$, in which, the hydrazide is present in the enolic form (L^- representing the enolate) with the Cl^- ion existing outside the first sphere of co-ordination. This has been confirmed by the disappearance of the band due to the co-ordinated >C=O group and the appearance of an intense band around 1590-1600 cm^{-1} due to the >C=N stretch appearing as a result of enolisation of the $-C(=O)NH-NH_2$ moiety to the imidol form $-C(OH)=N-NH_2$.

MoO_2^{+2} complexes of the Schiff bases :

The complexes of Schiff bases, obtained by the condensation of the carbonyl group of salicylaldehyde with the terminal $-NH_2$ of benzoylhydrazide, *o*-aminobenzoylhydrazide and *p*-aminobenzoylhydrazide, have the general formula $MoO_2(L'H)Cl$, where $L'H_2$ represent a molecule of Schiff base. In the Schiff base derived from *o*-aminobenzoylhydrazide, the condensation takes place from the ring amino-group of the hydrazide and is proved by the disappearance of the ring $-NH_2$ proton peak at 4δ[8] (as observed in the pmr spectrum of the hydrazide in $CDCl_3$) in the pmr spectrum (with TMS as standard) of the Schiff base in $CDCl_3$. In the complexes the ligands acted as monoprotic tridentate donors with the Cl^- occupying the sixth position in the co-ordination octahedra. In the complexes of Schiff bases derived from salicylaldehyde and the acidhydrazides, bonding takes place from the azomethine nitrogen, the carbonyl oxygen and the deprotonated phenolic oxygen[8]. MoO_2^{+2} complexes of the ligands obtained by condensing diacetylmonoxime with benzoyl, salicyl and *o*-aminobenzoylhydrazides have the general formula $MoO_2(L''H)Cl$. The IR data indicate that, in these complexes the bonding takes place from the hydrazide carbonyl oxygen, the azomethine nitrogen (indicated by a shift of ν>C=N from 1570-80 cm^{-1} to 1560-45 cm^{-1} region) and the oxime nitrogen (indicated by the shift of ν>C=N from 1425-35 cm^{-1} to 1475-45 cm^{-1} region)[9].

References

1. R. W. F. HARDY, R. C. BURN and G. W. PARSHALL, Inorganic Biochemistry, Vol I & II, Ed. G. L. EICHORN, Elsevier, 1975.

2. L. E. MORTENSON in S. P. COTOWICH and N. O. KAPLAN (Ed), Methods in Enzymology, Vol. 28, Academic Press, N. Y., 1972.

3. M. KELLY and G. LANG, *Biochim. Biophys. Acta*, 1970, **223**, 86.
4. G. N. SCHRAUZER and G. SCHLESINGER, *J. Amer. Chem. Soc.*, 1970, **92**, 1808.
5. PALMER, "Experimental Inorganic Chemistry", Oxford University, 1954, pp. 406-408.
6. JHONSON, LOCK and WILLIAMS, *Chem. Ind.* (London), 1968, 838 ; *J. Chem. Soc.*, 1964, 1054.
7. T. K. BANERJEE, Ph.D. Dissertation, Calcutta University, 1979.
8. B. C. KUNDU, Ph.D. Dissertation, Calcutta University, 1976.
9. S. SATAPATHY and B. SAHOO, *J. Inorg. Nuclear Chem*, 1971, **33**, 1313.

"Physicochemical Studies on the Composition and Stability of the Complexes of UO_2^{++} ion and Ag(I) with N-Glycylglycine"

R. S. SAXENA and S. P. BANSAL

Chemistry Department, Malaviya Regional Engineering College, Jaipur-4

Manuscript received 12 September 1979, accepted 30 November 1979,

ON account of the increased significance of the amino acids in pharmaceutical, biological and industrial field, considerable interest regarding their electrochemical behaviour has been shown in the past two decades. Saxena and co-workers have made extensive study on the electrometric behaviour of some of the amino acids[1-2]. This communication reports the polarographic determination of the stability constants of the complexes of UO_2^{++} ion with N-Glycylglycine and also the determination of composition and stability constants of Ag(I) complexes of N-Glycylglycine at 30° and 40° by potentiometric and conductometric titration techniques. There is, however, no reference in the literature on the study of the present system.

Experimental

N-Glycylglycine was supplied by B.D.H. chemicals Poole England and all other chemicals used were of AnalR grade.

In case of the polarographic study of N-glycylglycine complexes with uranyl ion, the concentration of UO_2^{++} ion was 1 mM in the presence of 0.1*M* $NaClO_4$ and 0.002% Triton X-100. The concentration of ligand was varied from 0.02 to 0.13*M*.

Toshniwal polarograph in conjunction with a thermostated H-cell was used for recording the current voltage curves. The capillary used had the following characteristics in 0.1 *M* $NaClO_4$: m = 2.953 mgm/sec, t = 2.5 sec/drop, h = 44.0 cms and −0.4 V vs S.C.E.

*p*H measurements were made on a Toshniwal *p*H meter (Type CL-46) with a glass electrode assembly.

Conductance was measured on electronic eye type conductometer (L.B.R. ; W.T.W. Germany). The temperature was controlled by a Universal thermostat (type U_3).

Results and Discussion

Polarographic Study :

The current-voltage curves of UO_2^{++} ion in presence of different concentrations of N-glycylglycine are plotted at 30°. In each case a single well defined cathodic wave appeared. All the plots of log $(i/i_d - i)$ vs $-E_{de}$ yielded straight lines and the slopes agreed with the reversibility of the reduction. The cathodic shift in $E_{1/2}$ coupled with decrease in diffusion current on increasing N-glycylglycine concentration shows the complex formation with UO_2^{++} ion. The plot of i_d vs $\sqrt{h_{eff}}$ was found to be linear indicating the diffusion controlled nature of the reduction of UO_2^{++} complexes of N-Glycylglycine.

The curvature obtained in the plot of $-E_{1/2}$ Vs. $-\log C_x$ showed the successive complex formation and hence the method of DeFord and Hume[3,4] was adopted for deriving various functions $F_j(X)$: From the experimental data, the complexity function $F_j(X)$ which is polynomial in (X), is set up ; the coefficients of the latter are required β_n. The graphical extrapolation reduces the polynomial equation to N-equations from which the corresponding β_n are obtained and are given below :

UO_2^{++}-N-glycylglycine complexes at 30°
$\beta_1 = 1$, $\beta_2 = 280$.

Potentiometric Studies :

The stoichiometry of the reaction between Ag^+ and N-glycylglycine were determined by potentiometric titrations of mixtures of the reactions in various ratio against standard NaOH (0.1*M*).

Addition of an equimolar concentration of Ag^+ greatly alters the shape of the free ligand titration curve (Fig. 1) as a result of complex formation and consequently a considerable lowering in buffer region starts. The inflection at m = 1 suggesting the formation of 1 : 1 complex. When 2 moles of ligand are added to 1 mole of Ag^+ the inflection at one mole of NaOH per mole of metal ion again indicates the formation of 1 : 1 complex.

Fig. 2 represents the change in conductivity when solutions of ligand were titrated against $AgNO_3$ solution. The breaks in the titration curves suggest the formation of 1 : 1 complex.

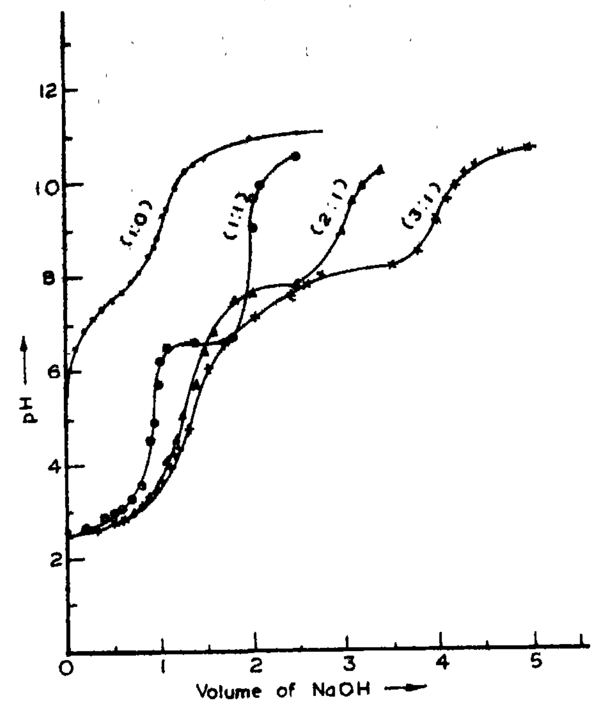


Fig. 1. Potentiometric titrations of Ag^+ in N-G.G. at ratios of N-G.G. : Ag^+ against NaOH (0.1*M*).

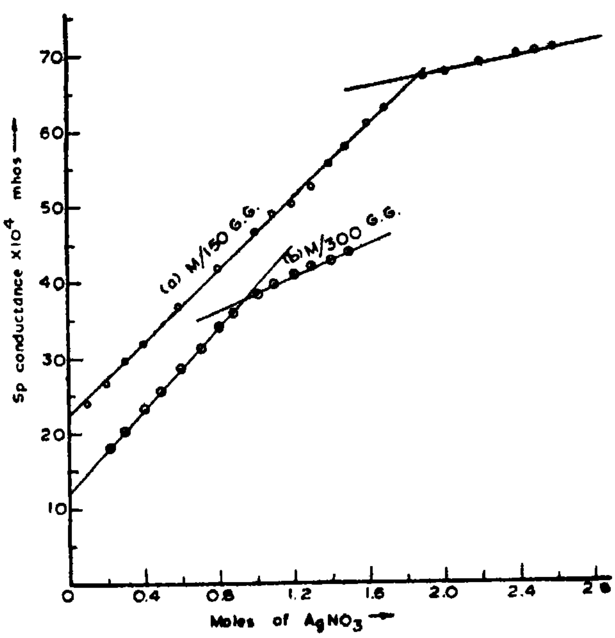


Fig 2. Conductrometric titrations of M/10 $AgNO_3$ against N-G.G.

Calvin and Melchior's extension[5] of Bjerrum's method[6] has been employed for the determination of stability constants of the complexes. The *p*H titrations of N-glycylglycine at ionic strength 0.1*M* KNO_3 and $HClO_4$ (2 mM) for initial lowering of buffer region in absence and presence of metal ion were carried out at 30° and 40° against 0.1*M* NaOH and the concentration of bound ligand, calculated from the horizontal distance between the corresponding curves, was divided by the metal ion concentration to obtain formation function $\bar{n}$. At any *p*H, the value of free ligand concentration (A) was calculated from the relation

$$[A] = \frac{[\text{N-GG}]_{Total} - [\text{N-GG}]_{Bound}}{[H^+]K_a + 1}$$

Here N-GG = N-glycylglycine.

where K_a is the dissociation constant of N-glycylglycine[7] is 8.5×10^{-9}. The formation curves obtained at different temperatures by plotting $\bar{n}$ vs. $-\log(A)$ reveal the formation of 1 : 1 complex. The log K values were read directly from the graph at $\bar{n} = 0.5$ and found to be 8.01 and 8.055 at 30° and 40° respectively.

Acknowledgement

The authors are thankful to C.S.I.R., New Delhi for the grant of research fellowship to one of them (S.P.B.) and to the Principal for providing research facilities.

References

1. R. S. Saxena and G. L. Khandelwal, *Indian J. Chem. Soc.*, 1977, **15A**, 757.
2. R. S. Saxena and M. C. Saxena, *Monatshefte für Chemie*, 1977, **108**, 829.
3. D. D DeFord and D. N. Hume, *J. Amer. Chem. Soc.*, 1951, **73**, 582.
4. D. N. Hume, D. D. DeFord and G C. B. Cave, *J. Amer. Chem. Soc.*, 1951, **73**, 5323.
5. M. Calvin and N. C. Melchior, *J. Amer. Chem. Soc.*, 1948, **70**, 3270.
6. J. Bjerrum, Metal Ammine Formation in Aqueous Solutions, P. Haase & Sons, Copenhagen, 1941.
7. E. Arthur Martell & Robert, M. Smith, "Critical Stability Constants", Vol. I, Aminoacids, Plenum Press (New York & England).

Ti(IV), Zr(IV), Hf(IV), Th(IV), Co(II), Ni(II) and Cu(II) Complexes of Vanillideneanthranilic Acid and Vanillidenebromoanthranilic Acid

JESSY CHACKO and GEETHA PARAMESWARAN*

Department of Chemistry, University of Calicut, Calicut 673 635

Manuscript received 21 August 1979, accepted 30 November 1979

METAL chelates of the Schiff bases have been recently reviewed by Holm *et al*[1]. Copper acetylacetoneanthranilic acid[2], copper N-(2-hydroxy-1 naphthalidene) anthranilic acid[3],

N-bromosalicylideneanthranilic acid complexes of Fe(II), Co(II), Ni(II), Cu(II), Zn(II)[4] etc were recently prepared. In this preliminary communication we report the synthesis of several metal complexes of Schiff bases derived from vanillin and anthranilic acid or bromoanthranilic acid. It may be mentioned that this is the first report on the metal complexes of these ligands and we wish to make a comprehensive study of the co-ordination complexes of these ligands with various transition metal ions.

Preparation of Vanillideneanthranilic Acid :

A mixture of alcoholic solution of vanillin (1.52 g) and anthranilic acid (1.36 g) was refluxed for 1 hour. It was allowed to cool, water was added and the solution was left overnight in a refrigerator for crystallisation. Fine shining yellow crystals which were separated, were recrystallised from 1 : 1 ethanol and preserved in a vacuum desiccator. m.p. 174°.

Metal Complexes : These were prepared by refluxing a mixture of the metal chloride and the ligand in appropriate molar ratio in suitable solvents for about 5-6 hours. The solid complexes were filtered, washed with dry ethanol or ethyl acetate and dried in vacuum desiccator. Since most of these complexes have a low solubility in common organic solvents they were purified by subjecting to soxlet extraction in dry ethanol and dried in vacuum.

Based on elemental analysis the metal complexes display 1 : 2 or 1 : 1 stoichiometry and may possess the composition ML_2X_2 or $(MLX)_2$. The magnetic moments indicate the presence of 3, 2 and 1 unpaired electrons in Co(II), Ni(II) and Cu(II) and the remaining complexes were found to be diamagnetic. From these values it is apparent that Ti, Zr, Hf and Th complexes possess monomeric octahedral structure whereas the remaining planar complexes may exist as dimers. Negligibly small conductance values of the compounds suggest them to be non-electrolytes.

The presence of the γ(OH) stretch in the infrared spectra of the complexes indicate the monobasic character of the ligands. In the complexes $\gamma C=O$ and $\gamma C=N$ were shifted to lower frequency side due to complexation. As the complexes are insoluble in common solvents it was not possible to find out molecular weights and degree of polymerisation of the complexes.

Further studies in N.M.R, E.P.R, T.G.A, etc. are in progress and details will be reported in due course.

Acknowledgement

The authors wish to thank Professor S. S. Moosath for providing necessary facilities. The authors are thankful to the University Grants Commission, New Delhi for awarding a fellowship to J. C. and financial assistance to G. P.

References

1. R. H. Holm, G. W. Everett (Jr.) and A. Chakravorthy, *Progress in Inorg. Chem.*, 1966, 7, 83.
2. R. K. Mehta, R. K. Gupta and S. L. Pania, *Talanta*, 1972, 19, 687.
3. R. K. Mehta, V. C. Singi and S. L. Pania, *J. Indian Chem. Soc.*, 1978, 50, 658.
4. G. C. Shivahare and D. Shankar Rao, *J. Indian Chem. Soc.*, 1974, 51, 785.

Complexes of Cu(II) and Cd(II) with Tetradentate Schiff's Bases

BIPIN B. MAHAPATRA, S. S. DASH, S. K. PUJARI

Chemistry Department, Panchayat College, Bargarh, Sambalpur, Orissa

and

S. GURU

Chemistry Department, Revenshaw College, Cuttack, Orissa.

Manuscript received 24 July 1979, accepted 30 November 1979

WE have been trying to synthesize new polydentate ligands in order to achieve rare co-ordination numbers through complexation of these ligands with some common divalent metal ions. In our earlier attempts, we have reported[1-4] complexes of a tridentate ligand, tri and tetradentate Schiff's bases using benzoin as the basic nucleus. In the present communication we have extended our investigation to the preparation of Cu(II) and Cd(II) complexes with tetradentate Schiff's bases derived from benzoin and ethylenediamine and *o*-phenylenediamine.

The method of preparation of the Schiff's bases have been mentioned in our earlier communication. Ethanolic solution of Cu(II) and Cd(II) chlorides were reacted with the Schiff's bases in 1 : 1 ratio followed by dropwise addition of ammonia with constant stirring when metal chelates separated out. These are filtered, washed with ethanol followed by ether and dried *in vacuo*.

Metal and nitrogen were estimated by standard methods. Conductance was measured in M/1000 acetone solution using Toshniwal conductivity Bridge. Magnetic susceptibility was measured on the solid specimen by Gouy method. IR spectra were recorded on KBr phase using Beckman IR-12 spectrophotometer. Electronic spectra were recorded on a Hilgerwatt uvispeck spectrophotometer with M/100 (Chloroform ligand) solution of the complexes. The relevant analytical conductance

and magnetic susceptibility data are recorded in Table 1.

Table 1—M.P. Analysis, Conductance and Magnetic Susceptibility Data

Compound	M.P. °C	%metal Found	%metal Reqd	%Nitrogen Found	%Nitrogen Reqd	Λ_M Ohm⁻¹ cm²	μ_{eff} B.M.
[CuL]	174	12.15	12.46	5.34	5.49	8.0	1.78
[CuL']	158	11.07	11.89	4.86	5.02	8.5	1.75
[CdL]	197	19.82	20.18	4.89	5.01	9.0	—
[CdL']	184	18.29	18.53	4.37	4.61	10.5	—

LH_2 and $L'H_2$ = Schiff's bases derived from benzoin and ethylenediamine and *o*-phenylenediamine respectively.

Results and Discussion

Complexes reported in the present investigation have the composition [ML] and [ML'] where M = Cu(II), Cd(II) and LH_2 and $L'H_2$ are Schiff's bases derived from benzoin with ethylenediamine and *o*-phenylenediamine respectively. Copper complexes are green and cadmium complexes are white in colour. All the four complexes have low melting points and are fairly soluble in acetone, having low conductance values (Table 1) indicating non-electrolytic nature of the complexes.

The Schiff's bases can function as tetradentate ligands using two hydroxyl oxygens and two imino nitrogen atoms as the bonding sites. Assignments have been made for the two principal bands, i.e. ν(C−O) and ν(C=N) in the IR spectrum. In the ligands the appearance of a band at 1210 cm^{-1} due to ν(C−O) has shifted down to 1200 cm^{-1} in the complexes. The ν(C=N) band has appeared at 1600 and 1590 cm^{-1} which has shifted to lower frequency region for complexes [ML] and to higher frequency region for complexes of the type [ML']. However, conclusive evidence regarding the bonding of nitrogen and oxygen atoms have been provided by occurrence of ν(M−N) and ν(M−O) around 515 and ~440 cm^{-1} respectively in the complexes[5].

In the electronic spectra of Cu(II) complexes one broad band appears around 15000 region indicating a planar configuration for these complexes. Magnetic moment values of the Cu(II) complexes indicate the presence of one unpaired electron. From the analysis conductance and IR spectral studies of Cd(II) complexes are found to be four co-ordinated having a tetrahedral environment around the metal ions.

References

1. B. B. Mahapatra, B. K. Mahapatra and S. Guru, *Acta Chimica* (Hungary), 1977, **94**, 191.
2. B. B. Mahapatra, B. K. Mahapatra and S. Guru, *J. Inorg. Nuclear Chem.*, 1977, **39**, 2291.
3. B. B. Mahapatra, B. K. Mahapatra and S. Guru, *J. Inorg. Nuclear Chem.*, 1978, **40**, 134.
4. B. B. Mahapatra, B. K. Mahapatra and S. Guru, *Indian J. Chem.*, Accepted.
5. J. R. Ferraro, "Low Frequency Vibrations of Inorganic and Co-ordination Compounds", Plenum Press, New York, 1971.
6. A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam, 1968.

Study of Camoquin-Ferrous Sulphate Complex

S. S. Gupta, S. Siddiqui and R. Kaushal*

Chemical Laboratories, Motilal Vigyan Mahavidyalaya, Bhopal (M. P.)

Manuscript received 19 August 1976, revised 17 January 1978, accepted 30 November 1979

CAMOQUIN is more active than quinine against malaria. In continuation of our work[1-4] on the metal complexes of antimalarials, herein we describe camoquin-ferrous sulphate complex.

Experimental

Composition of the Complex :

(a) Standard solutions of ferrous sulphate (0.01 *M*) and camoquin base (0.005 *M*) were prepared in spectroscopically pure 80% methanol. 5 ml of the ligand was diluted to 200 ml and titrated against the metal solution using 'Toshniwal' conductivity bridge and dip type electrodes at 19°. The analysis of conductance data reveals that a 1 : 2 complex is formed in solution.

(b) The nature of the complex was studied spectrophotometrically on 'Spekol' using Vosburgh and Cooper[5] Method. Mixtures containing 2 : 1, 1 : 1 and 1 : 2 proportions of equimolar solutions of ferrous sulphate and camoquin (5×10^{-4} *M*) in spectroscopically pure methanol were taken. The plot of absorbance vs wavelength is given in Fig. 1.

(c) Formation of 1 : 2 complex was further confirmed by the following :

(i) *Job's Method*[6], (ii) *Mole ratio Method*[7] and (iii) *Slope ratio Method*[8].

Isolation and Analysis :

Camoquin base 1.0 g (1 *M*) was dissolved in methyl alcohol and ferrous sulphate 1.56 g (2 *M*) was dissolved in minimum quantity of methyl alcohol with two drops of sulphuric acid were mixed slowly to ferrous sulphate solution with constant stirring when a chocolate coloured complex was obtained immediately. It was cooled in an ice bath for four hours, filtered, washed with methyl alcohol and dried on porous plate ; yield 1.7 g. No attempt was made to prepare 1 : 1 complex.

* Retd. Scientist, Holkar Science College, INDORE (M.P.).

Found : Fe, 15.09 ; SO_4, 25.83 ; N, 5.28 and H_2O, 10.09 ; while $C_{20}H_{22}ClN_3O.(FeSO_4)_2.4H_2O$ requires : Fe, 15.27 ; SO_4, 26.26 ; N, 5.74 and H_2O, 9.84.

Results and Discussion

The conductometric titration results clearly indicate that camoquin forms 1 : 1 and 1 : 2 complexes with ferrous sulphate ; while Fig. 1 indicates that only one complex is formed. The spectrophotometric studies by (i) Job's method, (ii) Mole ratio method and (iii) Slope ratio method also indicate that the complexation takes place in the ratio 1 : 2. The analytical data agree with the composition $C_{20}H_{22}Cl\ N_3O.(FeSo_4)_2\ 4H_2O$.

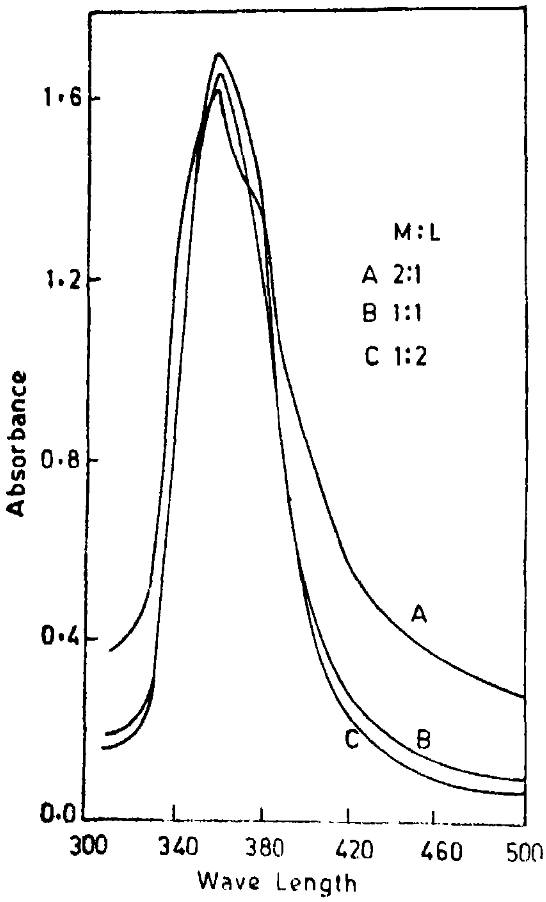


Fig. 1

The stability constants calculated by Job's and Yoe and Jones' method are 7.85 and 7.98 respectively. The free energy change ΔF has been calculated by the expression $\Delta F = -2.303$ RT log K. The results are -10.81 and -11.06 K cals mole^{-1} respectively.

The I.R. spectra of the ligand and complexes were recorded on Perkin-Elmer Model 237 spectrophotometer using KBr disc. Metal-nitrogen and metal-oxygen absorption bands were observed at 655 and 680 cm^{-1} respectively, while no such absorption bands were present in the ligand. Bonded sulphate shows strong absorption band at 1205 cm^{-1}. Band at 815 cm^{-1} and 1655 cm^{-1} indicate that co-ordinated water molecules are present in the complex. NH bending 1110 cm^{-1}, weak in parent compound becomes intense or modified to 1120 cm^{-1} on complexation indicating metal-NH co-ordination. $-C-N$ stretching vibrations of aromatic secondary amine is modified from 1260 to 1270 cm^{-1} on complexation ; while $C=N$ stretching vibration of ligand is modified from 1630 (weak) to 1640 (strong) on complexation. NH stretching of secondary aryl amine increases on complex formation from 3230 to 3340 cm^{-1}.

It may be mentioned that I. R. spectra of the complex show characteristic absorption bands of phenolic OH group namely 10 0, 1205 and 1355 cm^{-1}. No unambiguous conclusion is possible regarding the structure of the complex.

Acknowledgement

Authors are thankful to the Principal of the Motilal Vigyan Mahavidyalaya, Bhopal for providing the necessary facilities and to U.G.C. for financial support.

References

1. S. S. GUPTA and R. KAUSHAL, *J. Indian Chem. Soc.* 1974, **51**, 649.
2. S. S. GUPTA and R. KAUSHAL, *J. Indian Chem. Soc.*, 1975, **52**, 642.
3. S. S. GUPTA, S. SIDDIQUI and R. KAUSHAL, *J. Indian Chem. Soc.*, 1974, **51**, 769.
4. S S. GUPTA, S. SIDDIQUI and R. KAUSHAL, *J. Indian Chem., Soc.*, 1976, **53**, 242.
5. W. C VOSBURGH and G. R. COOPER, *J. Amer. Chem. Soc.*, 1941, **63**, 437 , 1942, **64**, 6330.
6. P. JOB, *Ann. Chim.*, 1928, **10**, 113 ; 1936, **10**, 97.
7. J. H. YOE and H. L. JONES, *Ind. Eng. Chem. Anal. Ed.*, 1944, **16**, 111.
8. A. E. HARVEY and D. L. MANNING, *J. Amer. Chem. Soc.*, 1950, **72**, 4488.

Studies on Complexes of Metal(II) Carboxylates with Donor Molecules : Part I. Complexes of Copper(II) Alkanoates with Aromatic Amine N-oxides and Triphenylphosphine Oxide

N. KUMAR, P. L. KACHROO and R. KANT

Department of Chemistry, University of Jammu, Jammu-180 001, India

Manuscript received 15 September 1978, revised 23 August 1979, accepted 19 November 1979

COPPER(II) carboxylates and their complexes with nitrogen donors have been intensively investigated because of their interesting structures and antiferromagnetic properties[1,2]. However, there is no

work done on the complexes of copper(II) alkanoates with aromatic amine N-oxides and related oxygen donors except some reports on the complexes of these ligands with copper(II) acetate[3-6]. We now report the preparation and characterisation of complexes of pyridine N-oxide (PNO), 3-methylpyridine N-oxide (3-MePNO), quinoline N-oxide (QNO) and triphenylphosphine oxide(TPPO) with copper(II) derivatives of propionic and *n*-butyric acids.

Experimental

Materials : Copper(II) propionate and *n*-butyrate were prepared by the standard method[7]. Their purity was established by metal analysis. PNO, 3-MePNO and TPPO were obtained commercially, while QNO was prepared by Ochiai's method[8]. The amine N-oxides were purified by vacuum distillation. Anhydrous TPPO was obtained by heating its hemihydrate at 110° for 3 hr and then by recrystallising from dry acetone.

Preparation of the Complexes : The complexes were prepared by the direct addition of the respective ligands to an acetone solution of copper(II) propionate or *n*-butyrate in 1 : 1 molar ratio. A representative preparation is given below :

Bis(propionato)pyridine N-oxide copper(II) : A solution of 0.62 g (0.0065 *M*) of PNO in acetone was mixed with a solution of 1.26 g (0.006 *M*) of copper(II) propionate in acetone (100 ml). The reaction mixture was concentrated under distillation to a volume of ~30 ml and filtered while hot. The filtrate, on standing overnight, deposited a crystalline solid which was separated, washed and then dried over phosphorus(V) oxide to yield 1.05 g of the required product. The analytical data of the complexes are listed in Table 1.

Analyses and Physical Studies : Copper was estimated gravimetrically as *bis*(pyridine)dithiocyanatocopper(II). Carbon and hydrogen were determined in the microanalytical laboratory of the department. Molar conductance of the complexes was determined on their millimolar solutions in methanol and nitrobenzene. Molecular weights were found by cryoscopic method in nitrobenzene. Magnetic measurements were made on powdered samples by Gouy's method. Electronic spectra of the complexes were scanned on Beckman DK-2A and Carl Zeiss DMR-21 spectrophotometers. Infrared spectra were recorded as nujol mulls on Perkin-Elmer-621 spectrophotometer.

Results and Discussion

The elemental analyses indicate that the complexes are of 1 : 1 stoichiometry and may be formulated as $[Cu(O_2CR)_2.L]$. The low molar conductance values of the complexes reveal them to be non-ionic in nature. The molecular weights of the complexes are consistent with their dimeric molecular formula weights. The magnetic moments of the complexes fall in the range 1.37-1.51 B.M. at room temperature, and are similar to those reported for dimeric addition complexes of copper(II) acetate with oxygen donors[5,6]. This suggests that the complexes have a dimeric, carboxylate bridged structure and involve some spin exchange between the two copper centres in each molecule.

The electronic spectra of the complexes in benzene exhibit two bands (I and II) in the regions

TABLE 1—ANALYSES, CONDUCTANCE, MOLECULAR WEIGHT, MAGNETIC AND ELECTRONIC SPECTRAL DATA

Complex (colour) yield%	Analysis% Found (calculated) Cu	C	H	Molar conductance	Molecular Weight Found (Calcd.)*	Magnetic moment B.M. (Temp.°K)	Electronic Spectral Data (cm^{-1}) Band I	Band II
$[Cu(O_2CC_2H_5)_2(C_5H_5NO)]_2$	20.81	43.35	4.85	25.60[m]	675	—	14,750[m]	—
(green) 57	(20.86)	(43.34)	(4.93)	0.051[nb]	(609)		14,125[b]	26,815
$[Cu(O_2CC_2H_5)_2(3\text{-}CH_3C_5H_4NO)]_2$	19.78	45.05	5.30	24.22[m]	—	1.37	14,770[m]	—
(green) 56	(19.95)	(45.21)	(5.34)	—	(637)	(292.5)	—	—
$[Cu(O_2CC_2H_5)_2(C_9H_7NO)]_2$	17.93	51.00	4.55	36.82[m]	676	1.38	14,410[m]	—
(yellow green) 58	(17.92)	(50.77)	(4.79)	0.069[nb]	(709)	(288.0	14,045[b]	25,840
							14,660[dts]	26,245
$[Cu(O_2CC_2H_5)_2(C_6H_5)_3PO]_2$	12.96	59.20	5.40	35.67[m]	1095	1.49	14,535[m]	—
(light green) 53	(13.03)	(59.07)	(5.13)	0.048[nb]	(975)	(288.0)	13,990[b]	25,775
$[Cu(O_2CC_3H_7\text{-}n)_2(C_5H_5NO)]_2$	19.19	46.70	6.25	26.40[m]	671	1.40	14,390[m]	—
(green) 60	(19.11)	(46.91)	(5.71)	0.057[nb]	(665)	(292.5)	14,165[b]	26,525
$[Cu(O_2CC_3H_7\text{-}n)_2(3\text{-}CH_3C_5H_4NO)]_2$	18.03	48.15	6.45	23.32[m]	—	1.38	14,340[m]	—
(green) 59	(18.34)	(48.48)	(6.06)	—	(693)	(293.0)	—	—
$[Cu(O_2CC_3H_7\text{-}n)_2(C_9H_7NO)]_2$	16.47	53.15	6.00	31.84[m]	855	1.40	14,410[m]	—
(yellow green) 66	(16.61)	(53.38)	(5.49)	0.074[nb]	(765)	(288.5)	14,470[b]	25,640
							14,620[dts]	25,975
$[Cu(O_2CC_3H_7\text{-}n)_2(C_6H_5)_3PO]_2$	12.16	60.45	6.05	29.30[m]	1067	1.51	14,430[m]	—
(light green) 58	(12.32)	(60.52)	(5.63)	0.051[nb]	(1031)	(289.0)	14,285[b]	25,975

* Calculated for dimeric formula.
m = methanol ; nb = nitrobenzene ; b = benzene ; dts = diffuse transmittance spectra.

13,990-14,450 and 25,640-26,525 cm^{-1} respectively. Band I, which appears, as a single broad band with a tail extending far into the near infrared region, is considered to originate from the copper(II) ion in a distorted octahedral environment and is assigned to $d_{xz}, _{yz} \rightarrow d_{x^2-y^2}$ transition[6]. Band II, however, appears as a shoulder on the lower energy side of the charge transfer band (O→Cu) occurring in the ultraviolet region and provides conclusive evidence in support of the proposed binuclear structure. The band is assigned to $d_{xy} \rightarrow d_{x^2-y^2}$ transition[6,9]. The electronic spectra of the complexes recorded in methanol show only band I. This obviously arises from the conversion of the dimeric complexes into monomeric species as a result of solvent co-ordination. The diffuse transmittance spectra of QNO complexes reveal little difference from those taken in benzene solution, suggesting thereby that these complexes have identical structure both in benzene solution and solid state.

The N–O stretching vibrations occurring at 1250 and 1278 cm^{-1} in PNO and 3-MePNO and the P=O stretching vibration occurring at 1189 cm^{-1} in TPPO undergo a negative shift of 17-30 and 8-9 cm^{-1} respectively in their complexes indicating that these ligands are co-ordinated to copper(II) through their respective oxygen atoms. In QNO complexes, however, the ν(N–O) is observed either at the same frequency (1232 cm^{-1}) as in the free ligand or is slightly shifted to higher wave numbers. This behaviour is typical of QNO-metal complexes and can be attributed to predominant $d_\pi - p_\pi$ back bonding from the metal to the ligand. However, δ(N–O) shows large positive shifts confirming the co-ordination of QNO to copper(II) through its N–O oxygen. The asymmetric and symmetric carboxyl stretching frequencies appear as sharp and intense peaks in the regions 1626-1619 and 1432-1416 cm^{-1} respectively. The position, nature and separation (~200 cm^{-1}) of these bands are characteristically similar to those of various 1 : 1 binuclear addition complexes of copper(II) acetate with oxygen donors[6]. All these investigations suggest that the complexes are binuclear carboxylate bridged species similar to that of copper(II) acetate monohydrate[10].

Acknowledgement

The authors wish to express their sincere thanks to Professor R. K. Dewan, Head of the Chemistry Department, University of Jammu, Jammu and Professor O. P. Vig, Head, Chemistry Department, Panjab University, Chandigarh for providing laboratory facilities. Thanks are also due to University Grants Commission, New Delhi for the award of a Junior Research Fellowship to R. K.

References

1. B. W. Jotham, S. F. A. Kettle and J. A. Marks, *J. Chem. Soc. Dalton Trans.*, 1972, 428.
2. R. J. Doedens, *Prog. Inorg. Chem.*, 1976, **21**, 209.
3. D. M. L. Goodgame and F. A. Cotton, *J. Chem. Soc.*, 1961, 2298.
4. S. J. Gruber, C. M. Harris, E. Kokot, S. L. Lenzer, T. N. Lockyer and E. Sinn, *Aust. J. Chem.*, 1967, **20**, 2403.
5. D. H. Hibdon and J. H. Nelson, *Inorg. Chim. Acta*, 1973, 7, 629.
6. J. J. McDougall, L. C. Nathan and J. H. Nelson, *Inorg. Chim. Acta*, 1976, **17**, 243.
7. R. L. Martin and H. Waterman, *J. Chem. Soc.*, 1957, 2545.
8. E. Ochiai and Sai Zai-Ren, *J. Pharm. Soc.*, Japan, 1945, **65**, 75 ; *Chem. Abs.*, 1951, **45**, 8526.
9. L. Dubicki and R. L. Martin, *Inorg. Chem.*, 1966, **5**, 2203.
10. J. N. Van Niekerk and F. R. L. Schoening, *Acta Crystallogr.*, 1953 **6**, 227 ; *Nature*, 1953, **171**, 36.

Syntheses of New Cobalt(III) Heterochelates Containing Three Different Bidentate Ligands in the Same Co-ordination Zone

A. SYAMAL* and P. K. MANDAL

Department of Applied Sciences and Humanities, Kurukshetra University, Kurukshetra-132 119 and Department of Chemistry, Regional Engineering College, Kurukshetra-132 119

Manuscript received 4 April 1979, revised 21 August 1979 accepted 19 November 1979

ALTHOUGH there has been considerable research interest in the syntheses and optical properties of cobalt(III) heterochelates of the type $[Co(AA)(BB)_2]^{n+}$ and $[Co(BB)(AA)_2]^{n+}$ (where AA≠BB= bidentate ligand) containing two different bidentate ligands in the co-ordination zone[1], very little is known about the cobalt(III) heterochelates of the type $[Co(AA)(BB)(CC)]^{n+}$ (where AA≠BB≠CC= bidentate ligand) containing three different bidentate ligands in the co-ordination zone. Only the complexes viz. $[Co(en)(tn)(tetramethylenediamine)]^{3+}$, $[Co(en)(tn)(neopentanediamine)]^{3+}$ and [Co(en)(oxalate) (glycine)] (where en=ethylenediamine and tn=trimethylenediamine) have been reported so far[2,3]. The syntheses of such heterochelates containing three different bidentate ligands are of interest due to the following reasons :

(a) The stability of the M-L bonding in the heterochelates may be favoured in comparison to that in the homochelates, (b) the chromophore system is amenable to variation, (c) novel magnetic and spectral properties may develop due to the variation in the ligand field strength, (d) novel distortion may be noticed, (e) the charge of the complex cation can be varied by proper choice of ligands, (f) the heterochelates may serve as models for the naturally occurring metal-ternary or

* Author to whom all correspondence should be directed.

TABLE 1—THE ANALYTICAL, ELECTRICAL CONDUCTANCE AND ELECTRONIC SPECTRAL DATA OF COBALT(III) HETEROCHELATES

Complex		%Co	%N	%Halogen	Λ_M ohm^{-1} cm^2 mole^{-1}	ν_{max} (ϵ) cm^{-1}
$[Co(en)(pn)(bigH)]I_3.H_2O^a$	Found :	8.2	17.9	55.1	428	20410(158),
	Reqd. :	8.5	18.2	55.0		28570(156)
$[Co(en)(pn)(acac)]I_2.H_2O^a$	Found :	10.1	9.7	45.1	259	20620(160),
	Reqd. :	10.5	9.9	45.0		26200(150)
$[Co(en)(pn)(picam)]I_3$	Found :	8.8	12.1	54.8	480	20200(150),
	Reqd. :	8.6	12.3	55.9		28985(180)
$[Co(en)(pn)(tn)]I_3$	Found :	9.0	12.8	57.7	430	20410(100)
	Reqd. :	9.1	13.0	58.8		
$[Co(en)(tn)(bigH)]I_3$	Found :	8.4	18.5	55.2	425	20200(125),
	Reqd. :	8.7	18.7	56.4		28980(155)
$[Co(en)(tn)(ophen)]I_3$	Found :	7.8	11.0	50.1	401	20410(71)
	Reqd. :	7.8	11.1	50.5		
$[Co(en)(tn)(dipy)]I_3.4H_2O^a$	Found :	7.2	11.0	46.9	420	21880(130)
	Reqd. :	7.4	10.5	47.5		
$[Co(en)(tn)(acac)]I_2$	Found :	10.0	9.8	45.1	260	21280(115)
	Reqd. :	10.5	9.9	45.0		
$[Co(pn)(tn)(ophen)]Cl_3$	Found :	11.8	16.9	21.4	420	20100(120),
	Reqd. :	12.0	17.0	21.6		28640(170)
$[Co(pn)(tn)(acan)]Cl_2.2H_2O^a$	Found :	12.1	14.0	14.1	235	20360(190)
	Reqd. :	12.0	14.3	14.5		

(a) Satisfactory H_2O analysis was obtained by heating the complexes at 110°C for one hr. The loss of H_2O at 110°C indicates that H_2O exists as water of crystallization.

quarternary systems. In this preliminary communication we report the syntheses of several new cobalt(III) heterochelates containing three different ligands in the co-ordination zone, the ligands used being en, tn, propylenediamine (pn), orthophenanthroline (ophen), 2,2′-dipyridyl (dipy), acetoacetanilide (acan), acetylacetone (acac), biguanide (bigH), 2-guanidinobenzimidazole (gbm) and 2-picolylamine (picam).

General Method of Synthesis of the Complexes :

Trans-$[CoCl_2(en)(tn)]Cl$[3] or *trans*-$[CoCl_2(en)(pn)]Cl$[4] or *trans*-$[CoCl_2(tn)(pn)]Cl$[4] (0.01 mole) was dissolved in water (*ca* 4 cm^3). The appropriate bidentate ligand (0.01 mole) was dissolved in water or 95% alcohol (10 cm^3) and added to the above solution. The *p*H of the solution was adjusted to 7 by 2*M* NaOH solution and the mixture was heated on a water bath for 1-2 hr. This was cooled and the *p*H was adjusted to 6.5 by 2*M* HCl solution. On cooling in ice bath for 1 hr. crystalline chloride compounds were obtained in case of less soluble complexes. In case of the complexes where the chloride salts are not isolable at this stage due to high solubility in water, a solution of KI was added to the solution which resulted in the precipitation of the iodide complexes. The separated chloride and iodide compounds were filtered, washed with cold water followed by 95% EtOH and dried under vacuum. In case of biguanide aqueous solution of biguanide hydrochloride was used.

The analytical, electrical conductance and electronic spectral data of the complexes are presented in Table 1.

The *trans*-$[CoCl_2(en)(tn)]Cl$, *trans*-$[CoCl_2(en)(pn)]Cl$ and *trans*-$[CoCl_2(pn)(tn)]Cl$ react with one molecule of bidentate neutral or monobasic ligand such as bigH, ophen, dipy, acan, acac, gbm, picam, en, pn, etc. and the heterochelates of the type $[Co(AA)(BB)(CC)]^{n+}$ (where $AA \neq BB \neq CC =$ bidentate ligand) are formed. These heterochelates are novel in the sense that these contain three different bidentate ligands in the same co-ordination zone. The complexes being cationic in nature is absorbed by cation exchange resin (amberlite IR 120, H^+) and the equivalent weight of the complexes was determined by passing an aqueous solution of the complex through the resin and then titrating the eluate with standard sodium hydroxide solution. The observed equivalent weight values agree well with the calculated values. The molar conductance values of the complexes in aqueous solution are given in Table 1 and the values indicate bi-univalent or tri-univalent nature[5] of the complex cations.

The electronic spectral data of the complexes are given in the Table 1. The complexes exhibit one or two spectral bands at around 20000 and 28000 cm^{-1} due to the spin—allowed transitions $^1T_{1g} \leftarrow {}^1A_{1g}$ and $^1T_{2g} \leftarrow {}^1A_{1g}$ respectively[6]. The high energy band cannot be located in some heterochelates as it is buried underneath the strong metal ligand charge transfer transitions. The complexes are diamagnetic as expected for six co-ordinate octahedral cobalt(III) complexes.

The isolation and characterization of other salts of the complex cations, chromatography, optical resolution and kinetics of dissociation of the

complexes are in progress and the details will be reported in due course.

Acknowledgement

The authors are indebted to the University Grants Commission, New Delhi-110 002 for the award of a Junior Research Fellowship to one of the authors (P. K. M.).

References

1. R. D. GILLARD and P. M. HARRISON, *J. Chem. Soc.*, A. 1967, 1657; A. R. GAINSFORD and D. A. HOUSE, *Inorg. Chim. Acta*, 1969, **3**, 367; K. IGI, T YASUD, J HIDAKA and Y. SHIMURA, *Bull. Chem. Soc.*, Japan, 1971, **44**, 426, M. TAKEUCHI and M. SHIBATA, *Bull. Chem. Soc.*, Japan, 1974, **47**, 2797, H. E. TOMA, *J. Inorg. Nuclear Chem.*, 1975, **37**, 785, K. YOSHIHIRA, *Bull. Chem. Soc.*, Japan, 1975, **48**, 2033.
2. J. C. BAILAR, JR. and J. B. WORK, *J. Amer. Chem. Soc.*, 1946, **68**, 232.
3. N. MATSUOKA, J. HIDAKA and Y. SHIMURA, *Bull. Chem. Soc.*, Japan, 1967, **40**, 1868, M. KOJIMA, Y. YAMADA, H. OGINO and J. FUJITA, *Bull. Chem. Soc.*, Japan, 1977, **50**, 2325.
4. A. SYAMAL and P. K. MANDAL, unpublished results.
5. M. M. JONES, Elementary Co-ordination Chemistry, Prentice Hall, 1964, p. 254.
6. F. A. COTTON and G. WILKINSON, Advanced Inorganic Chemistry, Second Edition, Wiley Eastern Pvt Ltd., 1966, p. 874.

Equilibrium Studies between Ni(II)/Cu(II), 8-Hydroxyquinoline-5-sulphonic acid and Histidine in Aqueous Solution

B. P. SINGH, H. S. VERMA and S. P. SINGH*

Department of Chemistry, J. V. College, Baraut-250 611 (India)

Manuscript received 12 September 1979, accepted 30 November 1979

8-HYDROXYQUINOLINE-5-SULPHONIC acid (HQSA) is well known chelating agent and its binary chelates have been studied quite extensively. However, so far the literature records very few solution equilibrium studies on the ternary complexes with HQSA as one of the ligands[1-6]. During the present investigations, the pH-metric studies of the systems, Ni(II)/Cu(II) – HQSA – histidine (His) have been made.

Experimental

Metal salts (nitrates, AnalaR BDH) solutions were prepared in doubly distilled water and standardized with disodium salt of EDTA using murexide as indicator. HQSA (Kodak) was recrystallized from water and weighed out directly for each investigation on account of its low solubility. Solution of histidine hydrochloride (BDH) was prepared by direct weighing and its strength was checked potentiometrically. Potentiometric titrations of the following solutions (total volume 50 ml): (i) 10 ml (0.025 *M*) ligand, (ii) 10 ml (0.025 *M*) ligand +10 ml (0.025 *M*), metal nitrate [M(II) – ligand, 1 : 1] where M(II) = Ni(II) or Cu(II) and (iii) 10 ml (0.025 *M*) each of primary and secondary ligands + 10 ml (0.025 *M*) metal nitrate [M(II) – primary ligand – secondary ligand, 1 : 1 : 1]; were carried out using a Systronics *p*H-meter. The ionic strength of the reaction mixtures was maintained approximately constant at 0.1 with potassium nitrate and the temperature at $30\pm1^\circ$ using a thermostate.

* To whom correspondence should be made.

Results and Discussion

The dissociation constants of HQSA ($pk_1=4.06$, $pk_2=8.49$) and His (6.05, 9.17) were taken from literature[4,7]. The *p*H-titration curves of solutions containing nickel nitrate and HQSA or His. HCl in equimolar proportions exhibit a sharp inflection at m = 2 (m = moles of base added per mole of metal ion or ligand), followed by the buffer regions in the high *p*H-range. However, in case of solution containing copper nitrate, two inflections at m = 2 and m = 3 are observed. The inflection at m = 2 in all cases indicate the formation of 1 : 1 complex. The inflection at m = 3, or buffer region indicates the conversion of 1 : 1 complex into hydroxo derivative. In all these cases precipitation starts at m ~ 2.

The *p*H-titration curves of solutions containing nickel or copper nitrate in presence of equimolar concentrations of HQSA and His. HCl exhibit a sharp inflection at m = 4, attributing the complete neutralization of both the protons of each of the ligands liberated as a result of chelation. All these curves run slightly above the corresponding 1 : 1 M(II)-HQSA titration curves in the beginning, which may be attributed to the presence of free tertiary and secondary amino groups in the His. HCl. This indicates that initially M(II)-HQSA (1 : 1) complexes are formed in the above systems. The lowering of these curves in comparison to the corresponding composite curves which is a measure of mixed ligand chelate formation, occurs after m = 1.5 in these systems, indicating the formation of the mixed ligand chelate species, which can only be 1 : 1 : 1 ternary complexes. The formation of the ternary complexes, thus, takes place in overlapping steps and through the formation of 1 : 1 M(II)-HQSA chelates. It also gets support by the analysis of the potentiometric data given below:

The formation of 1 : 1 : 1 mixed ligand chelate in the above systems may be represented as:

$$MA+H_2L^+ \rightleftharpoons MAL^- + 2H^+ \quad \ldots \text{(i)}$$

and the overall reaction for the formation of the 1 : 1 : 1 ternary chelate as ;

$$M^{2+} + H_2A + H_2L^+ \rightleftharpoons MAL^- + 4H^+ \quad \ldots \text{(ii)}$$

where M^{2+} stands for metal ion, H_2A for HQSA and H_2L^+ for His.HCl. If K′ and K″ are the equilibrium constants of reactions (i) and (ii) respectively, then

$$K' = \frac{[MAL^-][H^+]^2}{[MA][H_2L^+]} \quad \ldots (1)$$

and

$$K'' = \frac{[MAL^-][H^+]^4}{[M^{2+}][H_2A][H_2L^+]} \quad \ldots (2)$$

If T_M, T_A and T_L represent the total concentrations of the metal, the primary and secondary ligand species respectively and T_{OH} is the concentration of the base added to the reaction mixture during the titration and neglecting the concentrations of OH^-, A^{2-} and L^- in the *p*H-range studied, it follows that :

$$T_M = [M^{2+}] + [MA] + [MAL^-] \quad \ldots (3)$$

$$T_A = [H_2A] + [HA^-] + [MA] + [MAL^-] \quad (4)$$

$$T_L = [H_2L^+] + [HL] + [MAL^-] \quad \ldots (5)$$

$$T_{OH} + [H^+] = 2[MA] + 4[MAL^-] + [HA^-] + [HL] \quad \ldots (6)$$

In a 1 : 1 : 1 reaction mixture, using the equations (3)-(6) and relations for the dissociation constants of ligands and equilibrium constant (K_1) of the reaction, $M^{2+} + H_2A \rightleftharpoons MA + 2H^+$ it may be shown that :

$$a[M^{2+}]^2 + b[M^{2+}] - c = 0 \quad \ldots (7)$$

where $a = K_1(1+y)/[H^+]^2$, $b = x + y + 2xy$, $c = \{(4-m)T_M - [H^+]\}xy$, $x = 1 + k_1/[H^+]$ and $y = 1 + k'_1/[H^+]$

k_1 and k'_1 are the first dissociation constants of HQSA and His. HCl respectively. The values of K_1 ($\log K_{MA} = 11.92$ and 9.02 for Cu^{2+}-HQSA and Ni^{2+}-HQSA systems respectively) were taken from the literature[8].

The equilibrium concentration of the free metal ions present in the reaction mixture was determined by solving equation (7). The concentrations of other species involved in the equilibrium relations were then calculated from the above equations together with the values of equilibrium constants K′ and K″. Further, the formation constant of the ternary complex (K_{MAL}) which may be defined as :

$$K_{MAL} = \frac{[MAL^-]}{[MA][L^-]} = \frac{K'}{k'_1 k'_2} \quad \ldots (8)$$

and the overall stability constant of the mixed ligand chelate :

$$\beta_{MAL} = \frac{[MAL^-]}{[M^{2+}][A^{2+}][L^-]} = \frac{K''}{k_1 k_2 k'_1 k'_2} \quad \ldots (9)$$

The values of the equilibrium and chelate formation constants of the ternary complexes are presented in Table 1.

TABLE 1—EQUILIBRIUM AND CHELATE FORMATION CONSTANTS OF MIXED LIGAND CHELATES

($t = 30 \pm 1°$, $\mu = 0.1$ KNO_3)

System	$-\log K'$	$-\log K''$	$\log K_{MAL}$	$\log \beta_{MAL}$
Cu(II -HQSA-His	5.55±0.12	6.18±0.12	9.67±0.12	21.59±0.12
Ni(II)-HQSA-His	7.37±0.16	10.90±0.16	7.85±0.16	16.87±0.16

Other evidence supporting the formation of ternary complexes is also given by the colour change from the yellowish green of the 1 : 1 M^{2+}-HQSA binary complex and blue of the 1 : 1 M^{2+}-His binary complex to dark green in the presence of both the ligands. No precipitation at any stage in case of ternary systems also support the formation of ternary complexes.

References

1. B. J. INTORRE and A. E. MARTELL, *J. Amer. Chem. Soc.*, 1961, **83**, 3618.
2. G. A. L'. HEUREUX and A. E. MARTELL, *J. Inorg. Nuclear Chem.*, 1966, **28**, 481.
3. G. F. CONDIKE and A. E. MARTELL, *J. Inorg. Nuclear Chem.*, 1969, **31**, 2455.
4. S. P. SINGH and J. P. TANDON, *Monatsh Chem.*, 1975, **106**, 271.
5. S. P. SINGH and J. P. TANDON, *Acta. Chim. Acad. Sci. Hung.*, 1976, **88**, 385.
6. S. P. SINGH, H. S. VERMA and J. P. TANDON, *J. Inorg. Nuclear Chem.*, 1979, **41**, 587.
7. N. C. LI and R. A. MANNING, *J. Amer. Chem. Soc.*, 1955, **77**, 5255.
8. C. F. RICHARD, R. L. GUSTAFSON and A. E. MARTELL, *J. Amer. Chem. Soc.*, 1959, **81**, 1033.

A Rapid Method for Selective Separation and Estimation of Chromium in Some Ores and Alloys by Hydrated Zirconium Dioxide Ion-Exchanger

ASIT K. SEN and UDAY CH. GHOSH

Department of Chemistry, Visva-Bharati, Santiniketan-731 235 West Bengal, India

Manuscript received 11 August 1979, accepted 30 November 1979

TANDON *et al.*[1] reported the high K_d-value ($>10^4$) of chromium(VI) on hydrated zirconium dioxide which inspired us to study for selective separation of Cr(VI) from some ores and alloys using hydrated zirconium dioxide ion-exchanger.

In our previous work[8] with organic cation exchange resin Dowex-50W-X8, it was observed that Cr(VI) was reduced to Cr(III) by organic exchanger. Similar behaviour of Cr(VI) was indicated by earlier worker[4-6].

This paper reports systematic studies, rapid and selective recovery of Cr(VI) from some ores and alloys. No reducation of Cr(VI) takes place due to contact with hydrated zirconium dioxide ion-exchanger.

Experimental

Apparatus : A glass column (i.d. 1.2 cm) was used for column operation. 3.0 gms of hydrated zirconium dioxide (OH^--form) was taken in the column and flow rate was initially maintained at 1.5 ml/minute.

For *p*H measurement an ELICO *p*H meter model No. LI-10 was used. Analytical balance Awa. Labor type 707.04 (Germany) was used.

Reagents and Chemicals :

Zirconyl oxy-chloride was of reagent grade quality (Indian Rare Earth Co. Ltd.). All other reagents, were of AnalaR grade (BDH/E. Merck/Pfizer).

Extra low carbon alloy (Lot No. 1627 A) and DSP alloy steel (A) supplied by Durgapur Alloy Steel Plant, and B.A.S. Stainless Steel (69a) and chrome-iron ore (49f) were used.

Synthesis of Hydrated Zirconium Dioxide :

Hydrated zirconium dioxide was prepared by adding 0.1(*M*) aqueous ammonia to 0.1*M* zirconium oxychloride solution in 0.1(*M*) HCl (1 : 1 V/V) as described by Tandon *et al*[1]. The air dried product was grinded to 100-200 mesh size and ignited at 300° for an hour before use.

Distribution Co-efficients (K_d) of Cr(VI), Fe(III) and Ni(II) :

The chief constituents of the samples under investigation are nickel, iron and chromium. So the distribution co-efficients (K_d) of Ni(II), Fe(III) and Cr(VI) were determined as usual[6] at *p*H 1.5-2.0, adjusted with dilute HCl on hydrated zirconium dioxide exchanger by shaking 12 hours intermittently. The concentration of Ni(II), Fe(III) and Cr(VI) solutions were kept around $5 \times 10^{-4}(M)$. Fe(III) and Ni(II) in solutions were estimated by EDTA (disodium salt) titration[7] and Cr(VI) was estimated spectrophotometrically[7]. The K_d values were then calculated as before[6]. The K_d value of Ni(II), Fe(III) and Cr(VI) are 2.56, 0.71 and 1332 respectively.

Since hydrated zirconium dioxide acts as an anion exchanger at low *p*H, those K_d values are in quite agreement with what is expected. It is interesting to note that no reduction of Cr(VI) takes place in contact with the exchanger bed for a long period of time.

Elution : From preliminary elution studies of Cr(VI), Fe(III) and Ni(II), it is observed that Cr(VI) remains strongly adsorbed on hydrated zirconium dioxide (OH^--form) bed in dil HCl solution (*p*H 1.5) where as Fe(III) and Ni(II) percolate through the exchanger bed. On washing the exchanger column with 0.1*M* HCl (*p*H 1) Fe(III) and Ni(II) free from Cr(VI) are quantitatively collected in the effluent. The flow rate is kept at 1.5 ml/minute. After removal Fe(III) and Ni(II), Cr(VI) can be eluted quantitatively with 2.0*M* KOH solution.

Procedure : The ion-exchanger column (OH^--form) was treated with 40 ml of water at *p*H 1.5 (adjusted with dil HCl) before passing the test solution. A known volume of test solution was taken accurately and was passed through the exchanger bed at the flow rate of 1.5 ml/minute. The column was then washed with 60 ml of 0.1(*M*) HCl (*p*H 1). Fe(III) and Ni(II) were percolated out with the effluent and washing liquid. The adsorbed Cr(VI) was then eluted quantitatively with 60 ml of 2(*M*) KOH solution.

Results and Discussion

A synthetic mixture of ferro-chrome alloy, extra low carbon ferro-chrome alloy [Lot No. 1627 A], DSP alloy steel (A), B.A.S. stainless (69a) and B.A.S. chrome-iron ore (49f) were studied for selective separation and estimation of Cr(VI) by column chromatography. In the synthetic mixture, the amount of Fe(III) and Cr(VI) were varied from 1 : 10 to 10 : 1 in the ratio by weight. With the increase or decrease of the amount of Fe(III) in the mixture, the volume of washing solution is increased or decreased slightly. Similar results were observed in the eluant volume of Cr(VI) also. Fe(III) and Cr(VI) were estimated volumetrically[7]. Ni(II) was estimated with EDTA (disodium salt)[6]. In our previous work[8] it was observed that Fe(III) was adsorbed partly by hydrated stannic oxide exchanger during chrome-iron alloy analysis. But in this method no such adsorption of Fe(III) is occurred. So it is a better method for the analysis of chrome-iron ores and alloys than the previous one. This method is applicable also when Cr(VI) is present in the sample in microgram quantity. In that case Cr(VI) was estimated spectrophotometrically[9]. Hence, this method can be used to remove toxic Cr(VI) from polluted water. The results in Table 1 indicate that accuracy and precision of the recommended procedure is satisfactory. The method is simple, rapid and it takes only 2 hours time for complete analysis of chrome-iron ore.

TABLE 1—ANALYSIS OF FERRO-CHROME ORES AND ALLOYS

Sl. No.	Sample with composition	Metal analysed	Amount taken (mg)	Amount recovered (mg)	% of recovery	Standard Deviation
1.	Synthetic mixture	Fe	4.74	4.72	99.56	0.04
	Fe(III): Cr(VI)~1 : 10	Cr	48.38	48.61	100.60	0.3
2.	Synthetic mixture	Fe	47.26	46.98	99.40	0.25
	Fe(III) : Cr(VI)~10 : 1	Cr	5.06	5.09	100.60	0.08
3.	Synthetic ferro-chrome alloy Fe(III)-26%,	Fe	6.33	6.34	100.15	0.02
	Cr(VI)-72%	Cr	12.70	12.78	100.70	0.05
4.	Extra low-carbon ferro-chrome alloy (Lot No. 1627 A)	Fe	5.94	5.99	100.98	0.04
	Fe-26 88%, Cr-72.58%	Cr	12.33	12.16	98.60	0.20
5.	Stainless steel (69a)	Fe	35.60	34.73	97.60	0.80
	Cr-18.4%	Cr	9.34	9.45	101.2	0.13
	Ni-8.2%	Ni	3.67	3.69	100.60	0.01
6.	DSP alloy steel (A)	Fe	20.32	20.32	100.00	0.01
	Cr-23.75%	Cr	9.52	9 41	98.86	0.12
	Ni-20.41%	Ni	8.25	8.12	98.42	0.15
7.	Chrome-iron ore(49f)	Fe	1.60	1.59	99.40	0 01
	Cr_2O_3-43.1%	Cr	3.94	3.95	100 20	0.01
	FeO 15.3%					
8.*	Chrome-iron ore (49f)	Cr	10μg	9.9μg	99.00	0.08

* Exchanger taken -1.5g, column length (1.2 × 1.8) cm, Eluant volume -15 ml.

Acknowledgement

One of the authors (U.C.G.) is grateful to U.G.C. (India) for the award of a fellowship. Analysed ferro-chrome alloy (Lot No. 1627 A) and DSP stainless steel (A) from Durgapur Alloy Steel Plant is greatefully acknowledged.

References

1. N. J. SINGH and S. N. TANDON, *Talanta*, 1977, **24**, 459.
2. A. K. DE and A. K. SEN, *Talanta*, 1966, **13**, 1313.
3. F. Z. FROHLICH, *Z. Anal. Chem.*, 1959, **170**, 383.
4. K. ISAGAI and N. TAKESHITA, *Japan Analyst*, 1955, **4**, 222 ; *Chem. Abs.*, 1956, **50**, 11178 b.
5. D. A. SHISKOV, *Khin. Ind.* (Sofia), 1959, **31**, 113.
6. A. K. SEN and R. K. GHATUARY, *J. Indian Chem. Soc.*, 1979, **56**, 196.
7. A. I. VOGEL, "A Text Book of Quantitative Inorganic Analysis", Longman, London, 3rd Edn., 1962.
8. A. K. SEN and R. K. GHATUARY, *Z. Anal. Chem.*, 1979, **295**, 414.
9. E. B. SANDELL, Colorimetric estimation of traces of metals, Interscience, N. Y., 3rd Edn., 1965.

Thermolysis of Substituted Ortho-Hydroxy Acetophenone Oxime Complexes with Bivalent Metals-Part II

H. SINGH, U. K. RATHI*, P. DAS

Chemical Laboratories, D. S. College, Aligarh-202 001

and

D. KUMAR

Department of Agricultural Chemistry, N. P. G. College, Shikohabad, India

Manuscript received 24 September 1979, accepted 30 November 1979

ROLE of ortho-hydroxy keto oximes in the last one decade has encouraged the chemists due to their inevitable application[1-5] in various fields. The ineffable efficiency of these compounds is due to the presence of phenolic group in vicinity of keto oxime group to act as bidentate ligands with bivalent metal ions for the formation of six membered ring of stable chelates. This manuscript records the vivid TGA interpretation of palladium, nickel and copper complexes with 2-hydroxy-4-methyl-5-chloro acetophenone oxime, 2-hydroxy-5-chloro acetophenone oxime and 2-hydroxy-5-bromo acetophenone oxime.

Experimental

Synthesis of ligands :

The 2-hydroxy-4-methyl-5-chloro acetophenone oxime(HMCAOX) ; m.p. 146°, 2-hydroxy-5-chloro acetophenone oxime(HCAOX) ; m.p. 181° and 2-hydroxy-5-bromo acetophenone oxime(HBAOX) ; m.p. 169-170° were prepared as early reported[6].

The metal solutions were prepared by dissolving AnalaR grade metal chloride or sulphates in double-distilled water. The solutions of ligands were made in ethanol.

A Stanton thermobalance, model HT-SM range ambient 1600° with an accuracy of 1 mg was used for recording TGA at a heating rate of 5° per minute.

Preparation of complexes :

The complexes of palladium, nickel and copper were prepared by usual gravimetric method[7] at *p*H 0.6 to 0.9, 5.5 to 8 and 3.0 to 4.5 respectively employing the solution of aforesaid oximes. These complexes are non-electrolytic in nature and are soluble in common non-polar solvents.

Results and Discussion

Thermolysis of Pd(II), Ni(II) and Cu(II) complexes with HBAOX : It is obvious from

* To whom all correspondence should be made.

thermolysis curves (Fig. 1) that no loss in weight observed when all the complexes viz., Pd-HBAOX,

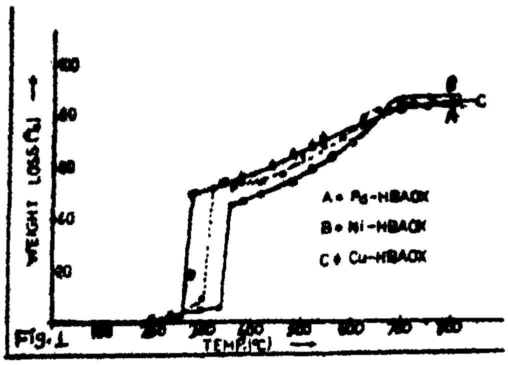


Fig. 1

Ni-HBAOX and Cu-HBAOX are heated up to 140° which is an indication that the chelates are non-hydrated in nature. The order of thermal stability was found as Cu-HBAOX (200°)>Pd-HBAOX (180°)>Ni-HBAOX(160°). In the complexes of Pd(II), Ni(II) and Cu(II) a rapid decomposition at 300°, 340° and 260° held with a weight loss of 39.0%, 55.0% and 49.5% respectively accompanied with a odour of disintegration products persists for days and furthermore the vapours are toxic when inhaled. The oxide formation is shown at 680° in nickel and 720° in copper complexes but in case of Pd-HBAOX the metal palladium is left at 640°. The thermal stability 200° of Cu-HBAOX is higher than Cu-salicylaldoxime, i.e., 140°.

It is evident from above thermogravimetric analysis that these chelates are as stable as chelates of resacetophenone oxime[8] but more stable than those of nioxime[9] and salicylaldoxime[10].

Therefore, it is concluded that 2-hydroxy-5-bromo acetophenone oxime (HBAOX) is a better thermogravimetric reagent for Pd(II), Ni(II) and Cu(II) than dimethylglyoxime, salicylaldoxime, nioxime and resacetophenone oxime, etc.

Thermolysis of Ni-HCAOX complex :

In view of the fate of this complex when subjected to the action of heat, a perfectly horizontal stretch is obtained up to 160° corresponds to the anhydrous $Ni(C_8H_7O_2NCl)_2$; this is well suited for the determination of nickel with an analytical factor (metal/metal-complex), i.e., 0.1746. A small weight loss in the temperature range 160-340° indicates the slow process of ignition of carbon. Beyond the temperature 340°, there is an abrupt weight loss of about 48.75% with a smoke and tenacious odour of disinfective product upto 360°, followed by a gradual loss in weight of 30.83% between 360-500°. After this temperature the organic matter disappeared and the final product is NiO at about 600° (Fig. 2).

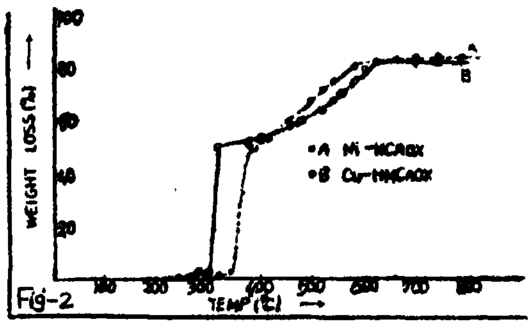


Fig-2

Thermolysis of Cu(II)-HMCAOX complex :

The stability of this complex upto 200°, reveals its anhydrous nature. There is very little loss upto 300° (Fig. 2) but above this temperature, the vigorous decomposition commences accompanied by a weight loss of 47.89% upto 320° with a choking odour. In the region 320-620° the gradual weight loss takes place due to the process of pyrolysis and the thermograms runs smoothly. Finally, at 640° the CuO is obtained.

All the thermolysis data are tabulated in the Table 1.

TABLE 1—PYROLYSIS DATA OF METAL COMPLEXES

Complex	Colour	Thermal stability Temp. (°C)	Decomposition Temp. (°C)	Approximate Temp. (°C) of residue formation	Possible residue	Residue%	
						Calcd.	Found
Pd-HBAOX	Yellow	180	300	640	Palladium metal	18.89	17.67
Ni-HBAOX	Green	160	340	680	NiO	14.95	13.57
Cu-HBAOX	Buff	200	260	720	CuO	15.25	15.98
Ni-HCAOX	Green	160	340	600	NiO	17.46	17.03
Cu-HMCAOX	Buff	200	300	640	CuO	17.27	16.76

Acknowledgement

We wish to express our thanks to Dr. S. S. Gupta, Principal, D. S. College, Aligarh for providing the requisite facilities and Agra University, Agra for JRF (UGC) to one of them (U.K.R.).

References

1. S. N. PODDAR, *Indian J. Appl. Chem.*, 1963, **26**, 153; 1964, **27**, 67.
2. D. B. INGLE and D. D. KHANOLKAR, *J. Indian Chem. Soc.*, 1978, **50**, 609 and 108.
3. M. DESAI, B. M. DESAI, B. S. PATWARI and M. H. GANDHI, *J. Indian Chem. Soc.*, 1973, **50**, 369.
4. U. K. RATHI, Ph.D. Thesis, Agra University, Agra.
5. Y. K. REDDY, *Proc. Indian Acad. Sci.*, 1965, **7A**, 368.
6. N. A. RAJU and K. NEELKANTAM, *Curr. Sci.*, 1950, **19**, 388.
7. A. I. VOGEL, "A Text Book of Quantitative Inorganic Analysis", Longman, 3rd Ed., 1968.
8. V. SESHAGIRI and S. BRAHAMJI, *Z. Anal. Chem.*, 1972, **262**, 275.
9. G. LIPTAY, E. M. PAPP and K. BURGES, *J. Inorg. Nuclear Chem.*, 1969, **34**, 247.
10. C. DUVAL, "Inorganic Thermogravimetric Analysis", Elseiver London, 1958, pp. 286, 259 and 347.

Chalcones XXIV : Studies on Chalcone Complexes of Fe(III) and Cr(III)

SHYAM SUNDAR MISRA, P. C. DWIVEDI*, R. K. UPADHYAYA **, V. P. SINGH † and D. R. GUPTA ††

Department of Chemistry, Feroz Gandhi College, Rae Bareli-229 001

Manuscript received 9 August 1979, accepted 30 November 1979

THE chalcones and their analogues are well known as multiprotecting agents +1-3. The field of coordination chemistry of these compounds has not been investigated widely[4]. However, 2-hydroxy chalcones are found[5-7] useful as gravimetric reagents for various cations. It is, therefore, thought worthwhile to undertake the synthesis, isolation and study of a few 3-d transition metal cation complexes, i.e., Fe(III) and Cr(III) with 8-hydroxy-5-quinolinyl chalcone. The complexes were prepared at an ionic strength of 0.005 mole in 90% aqueous methanol at boiling water temperature. The spectrophotometric and conductometric studies evaluated the stoichiometry of the complexes. The molecular conductance measurements were made with a view to study their stereochemistry. The characterisation of the complexes was done by elemental analysis. The I.R. spectra of the ligand 8-hydroxy-5-quinolinyl chalcone explores the possibility of chelation at –OH, >C=O and –C=N groups.

* Chemistry Department, H. B. T. I., Kanpur-208 002.

** Chemistry Department, University of Alfateh, Tripoli, (Libya).

† Chemistry Department, NREC College, Khurja, 203 131.

†† Chemistry Department, GBPUAT, PANTNAGAR, (U. P.) India.

Experimental

The solutions of metal nitrate of required strength were prepared in 90% aqueous methanol (v/v) of A.R. grade. The ligand 8-hydroxy-5-quinolinyl chalcone was obtained as reported 7 and purified by repeated crystallisations and its homogeneity was checked by T.L.C. Spectrophotometric studies were made by Bausch and Lomb spectronic-20. Conductometric measurements were made with Toshniwals conductivity bridge.

I.R. spectra was recorded in mujolmull with Beckmann spectrophotometer to study various important bands and the Gouy balance was used for the magnetic measurements. On the basis of spectrophotometric and conductometric results the stoichiometry of the complexes were found to be 1 : 3 metal ligand system. Double distilled water over alkaline potassium permanganate was used throughout the investigation and all the measurements were made at room temperature.

Isolation of the complexes :

The complexes were isolated by adding ligand solution to a hot methanolic solution of metal nitrates in the stoichiometric ratio of 3 : 1. The resulting dark coloured mixture was kept at about 50-60° over water bath with reflux condensor for about three hours, cooled filtered and the complex washed several times with cold absolute ethanol and finally recrystallised from dioxane.

Analysis :

Elemental analysis was performed by C.D.R.I., Lucknow and the metal components were determined gravimetrically[8]. The results are reported in Table I.

Results and Discussion

The conductometric titration gave the stoichiometric ratio of the ligand to metal as 3 : 1. The molar composition of the complexes were further determined by mole-ratio method and confirmed by their elemental analysis.

The magnetic measurements of Fe(III) and Cr(III) complexes were carried out at 303°K by Gouy method and the μ_{eff} values were found to be 1.37 and 1.01 BM respectively indicates the formation of high ligand field, low spin octahedral

TABLE 1

Sl. No.	Complex	Colour	Carbon %		Hydrogen %		Nitrogen %		Metal %	
			Cal.	Found	Cal.	Found	Cal.	Found	Cal.	Found
1.	$Fe(C_{18}H_{12}O_2N)_3$	Blue	73.62	74.20	4.10	4.00	4.78	4.98	6.37	6.58
2.	$Cr(C_{18}H_{12}O_2N)_3$	Dark blue	74.14	74.86	4.12	4.21	4.80	5.19	5.94	5.72

complexes with d^5 and d^3 systems having one unpaired electron only.

The molar conductance ($\wedge M$) values of the Fe(III) and Cr(III) complexes in dioxane was found to be 1.4 and 1.8 mhos respectively shows the non-electrolytic nature of the chelates. I. R. spectral data reveals that the lowering in $-OH$ and $-C{\equiv}N$ stretching frequencies at 3250 and 1665 cm^{-1} of parent ligand on complexation. This lowering indicates the participation of these groups in co-ordination. $>C=O$ group being at remorter position does not participate in the metal ligand interaction because the band corresponding to $>C=O$ groups remains imperturved during chelation. New bands appear in the ligand complexes with Fe(III) at 345 cm^{-1} and 436 cm^{-1} whereas in Cr(III) at 285 cm^{-1} and 423 cm^{-1} respectively fairly attributable to metal-oxygen and metal-nitrogen bonds which is in accordance with the results of Poddar and Das[9].

Taking into accounts the above results, most probable formula assigned to the complexes are.

$M(C_{18}H_{12}O_2N)_3$ where M = Fe(III) and Cr(III). Above structure satisfies maximum co-ordination number six for Fe(III) and Cr(III).

Acknowledgement

Thanks are due to authorities of H.B.T.I., Kanpur and C.D.R.I., Lucknow for providing necessary help and Dr. S. K. Sinha, Principal F. G. College for his keen interest.

References

1. K. K. HSU and F. C. CHEN, *Taiwan K. Hsue'h*, 1975, 27, 286.
2. S. S. MISRA, *Chinese Chemical Soc.*, 1977, 24, 45.
3. S. S. MISRA and D. R. GUPTA, *J. Indian Chem. Soc.*, 1978, 55, 412.
4. R. R. NAIDU, *Talanta*, 1975, 22, 614.
5. K. S. SUNDAR, *Curr. Sci.*, 1965, 34, 18.
6. B. NAVAN and A. K. DEY, *J. Indian Chem. Soc.*, 1975, 52, 1020.
7. S. S. MISRA and BHOLA NATH, *Indian J. App. Chem.*, 1971, 4, 260.
8. A. I. VOGEL, "A Text Book of Quantitative Inorganic Analysis", Longmann Group Ltd., London, 1969.
9. S. K. PODDAR and V. S. DAS, *Indian J. Chem.*, 1974, 12, [illegible].

Application of Radius Ratio Criterion to the Stability of Pyrochlore in Some Mixed Metal Oxide Systems

V. S. DARSHANE

Department of Inorganic Chemistry, Institute of Science, Bombay-400 032

Manuscript received 21 August 1979, accepted 30 November 1979

LITERATURE survey revealed that very little work is reported on pyrochlores where substitution of cations is carried out at A as well as B sites. Analysis[1] of natural pyrochlore minerals suggest that wide variety of both cationic and anionic substitutions are possible. Therefore, the systems $Y_{2-x}Ca_xTi_{2-y}Nb_yO_7$, $La_{2-x}Ca_xZr_{2-y}Nb_yO_7$ and $La_{2-x}Sr_xZr_{2-y}Nb_yO_7$ were studied by X-ray powder diffraction technique in order to investigate limits on the possibilities of ionic substitution (limiting radius ratio). Here it is observed that radius ratio criterion seems to be relatively unimportant in determining the stability limit for pyrochlore structure.

Pyrochlore compounds in which substitution of cations taking place either at A or B sites have been reported by various workers[2-11]. Pyrochlore structure has the general formula $A_2B_2O_7$ where A ions retain the eightfold co-ordination while B ions are only in sixfold co-ordination. Thus A ion is larger than B ion in the pyrochlore structure. The pyrochlore space group is found to be Fd3M-$O_h{}^7$ and there are eight $A_2B_2O_7$ formula units in the pyrochlore unit cell.

All the compositions mentioned in Table 1 were prepared by using standard ceramic technique and X-ray diffractometer patterns were taken on Philips X-ray machine using Cu K_α radiation with Nickel filter. The results of X-ray analysis are given in Table 1.

From Table 1 it is observed that in the systems investigated, the single pyrochlore phase is observed up to the compositions $Y_{1.6}Ca_{0.4}Ti_{1.6}Nb_{0.4}O_7$, $La_{0.8}Ca_{1.2}Zr_{0.8}Nb_{1.2}O_7$ and $La_{1.4}Sr_{0.6}Zr_{1.4}Nb_{0.6}O_7$. Knop *et al*[6] while studying pyrochlore titanates of the type $Y_{2-x}Ln_xTi_2O_7$ (where Ln = lanthanide ion from Sm to Lu) have observed the stability limit extending from Ahrens radius ratio of nearly 1.22 to 1.50. In the case of pyrochlore Stannates[7] they have reported the lower limit of $[r(A^{3+})/r(Sn^{4+})]$ 1.19 (Ahrens) and upper limit

TABLE 1

Formula	Radius ratio	Phases present
1. $Y_2Ti_2O_7$	1.353 (1.672)	Pyrochlore a=10.08 A
2. $(Y_{1-x}Ca_x)_2(Ti_{1-y}Nb_y)_2O_7$ x and y=0.2	1.370 (1.690)	Pyrochlore a=10.12 A
3. $(Y_{1-x}Ca_x)_2(Ti_{1-y}Nb_y)_2O_7$ x and y=0.3	1.380 (1.694)	Pyrochlore a=10.17 A + Calcium niobate (Monoclinic) trace
4. $Ca_2Nb_2O_7$	1.485 (1.760)	Monoclinic[12]
5. $La_2Zr_2O_7$	1.443 (1.689)	Pyrochlore a=10.80 A
6. $(La_{1-x}Ca_x)_2(Zr_{1-y}Nb_y)_2O_7$ x and y=0.6	1.438 (1.702)	Pyrochlore a=10.69 A
7. $(La_{1-x}Ca_x)_2(Zr_{1-y}Nb_y)_2O_7$ x and y=0.7	1.437 (1.713)	Pyrochlore a=10.57 A + Cal. niobate (trace)
8. $(La_{1-x}Sr_x)_2(Zr_{1-y}Nb_y)_2O_7$ x and y=0.3	1.492 (1.726)	Pyrochlore a=10.77 A
9. $(La_{1-x}Sr_x)_2(Zr_{1-y}Nb_y)_2O_7$ x and y=0.4	1.510 (1.756)	Pyrochlore a=10.75 A + $Sr_2Nb_2O_7$ (trace)
10. $Sr_2Nb_2O_7$	1.624 (1.953)	Monoclinic[13]

N. B. Radius ratios are calculated by using Ahrens radii for comparison with other workers while the values reported in parenthesis are obtained by using Shannon and Prewitt[14] ionic radii.

1.61. In calculating radius ratio Ahrens ionic radii are used for comparison with other workers. Similarly Wilson[11] has also calculated limiting radius ratio for 3-4 (valence of cation at A site is three while that of at B site is four) as well as 2-5 pyrochlores. It is between 1.18 and 1.63.

Now if the radius ratios reported by Knop and Brisse[6-7] and Wilson[11] are applied to the systems investigated in Table 1, then all the compositions except $Sr_2Nb_2O_7$ ($r_A/r_B = 1.624$) should have shown pyrochlore structure. From the systems investigated by Brisse it can be concluded that radius ratio rule applies fairly well, if the substitution is carried out either at A or B site but when the substitutions are carried out at A as well as B sites and ions of different charges are used, the radius ratio criterion does not apply. In fact use of ions carrying different charges (in order to compensate valence changes) should have induced fields with lower symmetry causing distortion of the pyrochlore structure. But it is observed that the structure is not distorted but at certain critical concentration, which varies from system to system, formation of solid solution is prohibited forming two distinct crystallographic phases. Therefore, it can be concluded that when cations of different charges and radii are substituted at both the sites, radius ratio criterion seems to be relatively unimportant in determining the stability limit for pyrochlore structure.

References

1. D. D. HOGARTH, *Can. Min.*, 1959, 6, 610.
2. F. JONA, G. SHIRANE and R. PEPINSKY, *Phys. Rev.*, 1955, 98, 903.
3. R. S. ROTH, *J. Res. Natl. Bur. Std.*, 1956, 56, 17.
4. E. ALESHIN and R. ROY, *J. Amer. Ceramic Soc.*, 1962, 45, 18.
5. L. H. BRIXNER, *Inorg. Chem.*, 1964, 3, 1065.
6. O. KNOP, F. BRISSE and L. CASTELLIZ, *Canad J. Chem.*, 1969, 47, 971.
7. F. BRISSE and O. KNOP, *Canad J. Chem.*, 1968, 46, 859.
8. A. W. SLEIGHT, *Mat. Res. Bull.*, 1968, 3, 699.
9. V. S. DARSHANE and V. V. DESHPANDE, *J. Indian Chem. Soc.*, 1973, 50, 761.
10. V. S. DARSHANE and V. V. DESHPANDE, *J. Indian Chem. Soc.*, 1973, 50, 229.
11. L. F. WILSON, Ph.D. Thesis, London University, 1958.
12. J. F. ROWLAND, N. F. H. BRIGHT and A. JONGEJAN, *Proc. 7th Ann. Conf. Ind. Appl. X-ray Analysis, Denver*, 1958.
13. K. SCHEUNEMANN and H. K. MULLER, *J. Inorg. Nuclear Chem.*, 1975, 37, 1679.
14. R. D. SHANNON and C. T. PREWITT, *Acta Crystallogr.*, 1970, B26, 1076.

3-Aldehydosalicyledene Cyanoacetyl Hydrazone as a New Reagent for the Spectrophotometric Determination of Ferric Ions*

K. K. PANDE* and J. V. LIKHAR

Chemistry Department, Govt. Science College, Gwalior, M. P.

Manuscript received 21 August 1979, accepted 30 November 1979

WHILE a number of compounds have been investigated as a reagent for the spectrophotometric determination of ferric ions. 3-Aldehydosalicyledene cyanoacetyl hydrazone (3-ASCAH) has not been investigated so far for this purpose. Fe^{3+}-3-ASCAH system was found to give stable reddish brown colour in acedic medium. The present article reports the use of 3-ASCAH as a new sensitive analytical reagent for the spectrophotometric determination of ferric ions at 370 nm in a *p*H range 4 to 5 and 50% ethanol-aqueous medium.

Experimental

Materials : All reagent and chemicals used in the present work were of Analar B.D.H. grade. Pure distilled water redistilled over alkaline permagnate and free from carbon dioxide, was used throughout the investigation.

Synthesis of Ligand : The 3-aldehydosalicylic acid and cyanoacetic acid hydrazide were prepared[1,2] and taken in equimolecular proportions in

* Presented at Indian Science Congress, 1979 (Part III-2, p. 1 in Abstract).

alcoholic medium. After refluxion for two hours, 3-aldehydosalicyledene cyanoacetyl hydrazone (3-ASCAH) separated as a crystalline compound. The deep yellow coloured needles of this Schiff base were purified by repeated crystallisation from alcohol. The compound is soluble in alcohol and dioxane with sharp m.p. 208°.

Apparatus: The absorbance measurements were done on Beckman DU spectrophotometer Model 109200 using a matched pair of 1 cm cuvettes. The Metrohm *p*H meter Model E-350A with wide range glass calomal electrode was used. Buffer solutions prepared of potassium hydrogen phthalate and borax were used for standardisation of the *p*H meter.

Stock Solutions:

Stock solution of 5×10^{-3} *M* of 3-aldehydosalicyledene cyanoacetyle hydrazone prepared by dissolving the requisite amount in ethanol. Standard solution of Fe(III) of 1×10^{-3}*M* was prepared in double distilled water and estimated by EDTA[3].

Sequence of Addition of Reagents: No change in the absorbance or colour intensity of the complex was observed if the order of addition of reactants was changed.

Absorbance Spectrum: A solution of 1 ml of Iron stock solution and 1 ml of 3-ASCAH was adjusted to *p*H 5 while diluting with water to exactly 10 ml maintaining the 50% aqueous-ethanol (v/v) medium. An appropriate blank was prepared in a similar manner except that water was added in place of Iron solution. Absorbance measurements were made in the region 350-600 nm after the adjustment of *p*H. The reagent showed a sharp absorbance band due to $Iron^{3+}$-3-ASCAH complex at 370 nm with the molar absorptivity of 1.292×10^{3} litres/mole cm.

Effect of pH: The absorption characteristics of the complex in the *p*H range 4-5 showed a maximum colour with 3-ASCAH. The *p*H was adjusted with buffer.

Conformity to Beer's Law:

A number of solutions containing varying amount of Iron and 0.2 ml of 5×10^{-3} *M* 3-ASCAH solution at *p*H 5 ± 0.1 were prepared and tested for the confirmation of the colour system for Beer's Law, which was seen to be followed at 370 nm over the concentration range 6 to 70 ppm of Iron for 1.0 cm cells; the absorbance readings were low below 6 ppm of Iron.

Sensitivity and Molar Absorptivity of the Complex: The spectrophotometric sensitivity of the colour reaction in terms of Sandell's definition[4] is 0.043 μg of Iron per cm^2 for log Io/I = 0.001. The molar absorptivity calculated from a plot of Beer's Law is 1.292×10^{3} litres/mol. cm. at 370 nm.

Effect of Diverse ions and Media: The effect of different inorganic and organic species was studied for solutions containing 10 ppm of Iron and 0.2 ml (5×10^{-3} *M*) of the reagent and the varying concentrations of each ion were tested in a total volume of 10 ml at *p*H 5. The absorbance measurements showed that Co^{2+}, Ni^{2+}, Cu^{2+} and Hg^{2+} interfere in this colour reaction even in small quantities. The presence of acetate ion in more than 0.01 *M* increases the error by 1.5%.

The alcohol contents must not be less than 35% (v/v), otherwise the reagent is precipitated.

Conclusion: 3-ASCAH may prove to be a versetile reagent for the determination and estimation of Iron spectrophotometrically in presence of several anions and cations.

References

1. J. DUFF and E. BILLS, *J. Chem. Soc.*, 1932, 1987.
2. D. CHAKRAVARTY, A. BOSE and S. BOSE, *Pharm. Sci.*, 1964, **53**, 1036-39.
3. F. J. WELCHER, The Analytical uses of EDTA. Von Nostrand, Princeton, 1951.
4. E. B SANDELL, Colorimetric Determination of Trace of Metals, Interscience Publishers, INC, New York, 1965.

A Novel Spray Reagent for Plant Pigments

K. P. TIWARI* and P. K. MINOCHA

Department of Chemistry, University of Allahabad, Allahabad

Manuscript received 7 September 1979, accepted 30 November 1979

THE present investigation was carried out with a view to find some new spray reagents for detecting the presence of hydroxyl groups adjacent to carbonyl groups in the quinones and flavones. This was achieved by paper chromatographic procedures involving the use of *n*-butanol : acetic acid : water $\left((4:1:5\ \frac{v}{v}\right)$ as solvent and 1% aqueous sodium vanadate as spray reagent when the plant pigments were present in amounts of at least 5μg each.

This reagent has shown better results on comparing with the following popular spray reagents[1-4] viz. ammonia vapours, *p*-toluene sulphonic acid, iodine vapours, methanolic aluminium chloride, methanolic sulphuric acid, 1%

Table 1

Substance	R_f	Colour observed	Fluorescence in U.V light
Taxifoline	0.78	LB	BL
Taxifoline-galactoside	0.73	LB	BL
Kaempferol	0.83	Y	DB
Quercetin	0.78	Y	DB
Rhamnetin	0.80	Y	BL
5,7-dihydroxy 4'-methoxy flavone	0.50	Y	BL
7-hydroxy flavone	0.00	—	BL
5,7-dihydroxy flavone	0.67	LY	LB
5,7',4'-trihydroxy 3,6,8'-trimethoxy flavonol	0.61	LY	LB
Avicularin	0.70	Y	LB
Quercitrin	0.82	Y	LB
Rutin	0.56	Y	LY
Penta methyl quercetin	0.71	—	BL
5-hydroxy 7,3',4'-trimethoxy flavonol	0.38	Y	DB
2-hydroxy 1 : 4 naphthaquinone	0.84	LB	BL
Chrysophanol	0.76	P	LB
Emodine	0.64	LP	LP
Physcion monomethyl ether	0.11	P	LP

methanolic sodium hydroxide, 5% aqueous sodium carbonate solution. Only ammonia vapours and 1% methanolic sodium hydroxide were found almost equal in performance in comparison to that of sodium vanadate. The new reagent is specific for the detection of hydroxyl group adjacent to carbonyl groups in quinones, flavones and their *o*-glycosides even at concentration of 5μg. The pigments having no hydroxyl groups adjacent to the carbonyl groups and completely methylated flavonoids do not give colour reaction with the reagent.

The R_f values, colour with the spray reagent and colour in the UV light are given in Table 1.

LB = Light Brown, BL = Bluish, Y = Yellow, DB = Dark Brown, LY = Light Yellow, P = Pink, LP = Light Pink.

Acknowledgement

The authors are thankful to Dr. M. Masood, University of Allahabad, who kindly supplied the authentic samples of some of the compounds reported in this paper. P. K. Minocha is also greatful to UGC, New Delhi, for a Junior Research Fellowship.

References

1. J. B. Harborne, T. J. Mabry and H. Mabry, 'The Flavonoids', Chapman and Hall, London, 1st. Ed., 1975, p. 24.
2. J. C. Kohli, *Ann. Chim.*, 1975, **10**, 323.
3. T. A. Geissman 'Modern Methods of Plant Analysis' edited by K. Peach and M. V. Tracey, Springer Verlag, Berlin, 1955, 3, 450.
4. J. C. Kohli and A. K. Arora, *Ann. Chim.*, 1972, **2**, 21.

J. Indian Chem. Soc.,
Vol. LVII, January 1980, pp. 112

Book Review

Inorganic Chemistry Concepts by P. L. Soni and Mohan Katyal
Published by Sultan Chand & Sons. Price Rs. 15.00

Chemistry text books for Honours School beginners used to be a domain of overseas authors. Recently many India teacher-authors are having their tries, and books of various prescriptions are trickling in. This is a good sign as there is always room for self-sufficiency and use of national talents. On such a consideration the publication of the book under review is welcome. The ambitious title of the book is in itself a challenge and it may be admitted it hardly matches the expectation for a conceptual introduction to modern inorganic chemistry. For one thing the structural aspects of inorganic compounds are missing. The familiar discussions on chapters such as atomic structure, bonding, electrode potentials, etc., fail to generate the right interest and neglect the overall relevance these have in the chemistry of elements. One is prone to the simplistic generalisation that this work has a compilation character-occassionally disjointed, sketchy in places and different chapters moving on and off the mark of a pre-set standard. Valence theories have been presented in a matter-of-fact way-a dangerous thing to do. Considering the overall level the book aims at S.I. units (p. 2-4), Linnett's theory (p. 168-172), Hard-soft concepts of acids and bases (p. 194-198) and electrode potential tables (p. 211, 212) for minerals are additions likely to confuse the beginners. While the authors' desire to be comprehensive is appreciable, the tome deserves more than the 200 odd pages presented. The authors' use of sentences are simple and unambiguous ; printing and general get-up are satisfactory. While many serious students and teachers alike will prefer the available familiar texts, the less diligent learners may fiind this book easy for their utalitarian purpose at the very cheap prize offered.

P. K. Das.

INFORMATION FOR AUTHORS OF CONTRIBUTIONS AND PUBLISHERS OF BOOKS

1. **Manuscripts for publication** in the *Journal of the Indian Chemical Society* should be typed with double spacing on one side of good quality paper with at least 3.5 cm margin on the left hand side and clear margin on all other sides ; ***the original and 2 carbon copies are to be submitted*. These should be addressed to the Honorary Editor, Indian Chemical Society, 92, Acharya Prafulla Chandra Road, Calcutta-700 009.**

On the top right hand corner of the title page of the manuscript, the **section** (viz. Inorganic Chemistry, Physical Chemistry, Organic Chemistry, Analytical Chemistry, Biochemistry, Industrial Chemistry/Chemical Engineering, etc.) for which the communication is to be considered **should be clearly indicated**.

On receipt of a paper the author sending the paper shall be duly intimated of the Society's registration number for the manuscript which must be quoted by the author in all future correspondence on it to the Society. *All such future correspondence should be addressed to the* **Executive Editor**.

2. **A paper will not be accepted for publication unless the author or at least one of the authors (in case of a contribution submitted jointly by more than one author) is a Fellow or a Member of the Indian Chemical Society of some category.**

3. Original contributions to new chemical knowledge, both experimental and theoretical, in all the areas of Chemistry, are accepted for publication in the *Journal of the Indian Chemical Society*. Two types of contributions are considered for publication : *Articles* and *Notes*. Both categories should have sufficient information to permit repetition of the experimental work.

Contributions which have been published or accepted for publication in another journal or in any other freely available printed work **will not be published** in the *Journal of the Indiun Chemical Society*. **A declaration to that effect from the author must accompany a manuscript submitted for publication.**

Authors are solely responsible for the factual accuracy of their contribution.

4. A prospective contributor should consult recent issues of this journal to get acquainted with its *contents* and *style*. Definitive accounts of significant completed studies presenting new important data or providing a fresh approach to an established subject should be submitted as **articles**. The presentation should be in a logical manner consistent with accuracy, clarity and brevity. The text should be divided into the following sections : (a) Introduction ; (b) Experimental ; (c) Results and Discussion ; (d) References. Divisions within the sections should be indicated by sub-headings. **Extensive review and unnecessary details of earlier work should be avoided.** Well known or previously published procedures followed in the experimental work should only be referred to omitting details. Important findings and results of much interest which may require priority in publication shall be considered for publication as **notes**.

Any portion of the text for which a special type of print is required must be indicated : **single underlining** for *italic* type and **double underlining** for *bold black* type.

The *title* of a contribution should tell accurately and clearly what the paper is about. The first letter of each noun and adjective in the title must be *in capital*. The title must be followed by the names of the authors and their addresses. The name of the senior author to whom correspondence may be made about the paper must be marked by an asterisk (*). His present address, if different from that quoted as above, must be given in a foot-note.

Every article must be accompanied by an informative *abstract* that summarizes the principal findings of the work presented in the paper. Normally it should not be over 3 per cent. of the length of the paper and should not exceed 250 words. It should be in a form that it may be used directly for publication in abstracting periodicals. This abstract should be typed before the main text and indented ca. 2 cm to the right of it. *No such abstract is necessary for notes.*

5. The charge carried by an ion should be indicated in the following manner : Na^+, Cu^{2+}, $Co(NH_3)_6^{3+}$ Cl^-, SO_4^{2-}, $Fe(CN)_6^{3-}$, etc. Standard abbreviations should be used throughout the experimental section : e.g., m.p., b.p., sec, min, hr, mg, g, kg, mm, cm, cps, tlc, uv, ir, nm, etc. Analytical

results should be reported in the form : (Found : N,......; Cl...... ; Ni,...... per cent. Calcd. for...... N,...... ; Cl,...... ; Ni,...... per cent.).

6. *Literature citations* should be numbered consecutively and these numbers are to appear as superscripts in appropriate positions in the text. Care must be exercised for uniformity in reference citations. "Ibid", "Idem", "et al", etc. should not be used. *Abbreviations for titles of journals must ordinarily conform to those used by the "Chemical Abstracts" published by the American Chemical Society (vide : "List of Periodical Abstracted").* **All the references must be typed in their serial order at the end of the text in the manuscript. The names (not surnames only) of all the authors should be given.** A few sample citations are noted below :

1. P. C. RAY, *J. Indian Chem. Soc.*, 1924, **1**, 207.
2. R. J. KULA, D. T. SAWYER, S. I. CHAN and C. M. FINLEY, *J. Amer. Chem. Soc.*, 1963, **85**, 2930.
3. C. S. GARNER and D. A. HOUSE in "Transition Metal Chemistry", (Ed.) R. L. CARLIN, Marcel Dekker, New York, 1970, Vol 6, p. 59.

Foot-notes must be referred to in the text with suitable symbols such as,*, †, ‡, §, ‖, etc.

7. **Instructions for Diagrams and Figures.** The number of tables, diagrams and photographs should not be more than what is absolutely necessary, in view of the fact that the reproduction of such materials is very costly. **If these exceed 20% of the pages of the text, authors may be asked to pay for the excess cost.**

a. Figures should be numbered with Roman numerals and mentioned consecutively in the text indicating their respective locations. *All Figures must have legends and these should be typed out separately in a sheet of paper at the end of the main text of the manuscript.* **Legends should not duplicate information in the text.**

b. One set of the drawings should be made with India ink on tracing cloth or good quality white drawing paper. *Gragh paper should not be used.* Lines should contrast sharply with the background. **Most drawings should be planned for reproduction to a column width of 7.5 cm. Lettering should be large enough to be 1.5 mm high after reduction.** Large drawings should be simplified, for submitting with the manuscript, in a size which is reducible to not more than 16 cm × 22 cm. For satisfactory reproduction all drawings should be approximately twice the size in which they are to appear in the print. Use of legends in the body of the diagram must be reduced to the minimum. Free hand drawings and drawings unsuitable for block making cannot be accepted. If necessary the Editors may get the figures redrawn properly for which the actual cost is to be borne by the author(s). Structures and formulae which cannot be composed must also be submitted as suitable drawings for blockmaking.

c. If original tracings are not available, glossy prints of the tracings can be used if the background is clear and the lines are distinct.

d. Photographs should be glossy black and white prints with sharp contrast. Paper clips mark the surface, and writing on the back of photos often punches through, spoiling the prints. **Photographs of equipment should be avoided.** Photomicrographs should be unmounted and should not be more than 7.5 cm. wide.

8. *Reprints* shall be supplied only on receipt of payment of the usual charges. i.e. 50 reprints @ Rs 10/- per page or part thereof, subject to a minimum charge of Rs 25/- ; 100 reprints of 1—2 pages @ Rs. 50/- and for subsequent 2 pages or part thereof @ Rs 40/- next 100 reprints or part thereof at half the original rate. *No free reprints are supplied and no such request can be entertained.* Reprint order form is sent to author with the proof.

9. **Books submitted for review** in the *Journal of the Indian Chemical Society* must be sent in duplicate to the Honorary Editor, Indian Chemical Society, 92, Acharya Prafulla Chandra Road, Calcutta-700 009, so that one copy may be retained in the Library of the Indian Chemical Society, while the other copy may be retained by the reviewer for his personal use.

In case of rejection of a paper, the opinion of the Honorary Editor shall ordinarily be treated as final.

AUTHOR INDEX

J. Indian Chem. Soc.,
Vol. LVII, February 1980, pp. 113-115

Some Mixed Ligand Complexes of Ni(II)

C. P. SAXENA
Chemistry Department Holkar Science College, Indore-452 001
and
P. V. KHADIKAR
Chemistry Department University of Indore, Indore-452 001

Manuscript received 31 July 1979, accepted 30 November 1979

Mixed ligand complexes of Ni(II) with para amino salicylic acid as primary ligand and pyridine, β-picoline, 8-hydroxyquinoline and nicotinic acid as secondary ligands were synthesised. The compounds have been analysed and structures have been *suggested on the basis of reflectance spectra, magnetic susceptibility* and I. R. spectral studies.

KHADIKAR and coworkers have carried out extensive work on the complexing tendency of salicylic acid and nuclear substituted salicylic acids with several metal ions. Complex formation with pyridine and substituted derivatives have also been studied and compounds with composition $[ML_4]^{++}$ and $[ML_6]^{++}$ have been reported[1-3]. In the present investigation adduct formation of pyridine, β-picoline, oxine and nicotinic acid with Ni(II) para amino salicylate has been attempted. The obvious interest in taking up this investigation is that besides synthesis, mixed ligand complexes are expected to provide valuable information on magnetic properties, electronic spectra, flexidentate behaviour of polydentate ligands nnd stereochemistry. Magnetic data aud reflectance spectra of these compounds are discussed on the basis of ligand field theory and the bonding in the compounds has been suggested on the basis of I.R. spectra.

Experimental

The mixed ligand complexes of Ni(II) with para amino salicylic acid (PAS) as primary ligand aud pyridine, β-picoline, oxine and nicotinic acid as secondary ligands have been prepared using the method described by Khadikar *et al*[4]. The composition of the complexes formed have been confirmed by elemental analysis and is given in Table 1.

Magnetic moments of all the compounds were determined at room temperature using Gouy Method[5] and are found as shown in Table 1. Reflectance spectra were recorded on spectrophotometer VSU-2P using 1 cm cell length. Observed band positions with assignments are given in Tables 2 and 3. Spectrochemical parameters for these complexes are given in Table 4. I.R. spectra of the isolated complexes were recorded by using Perkin

TABLE 1—ANALYTICAL DATA AND MAGNETIC MOMENTS

Sl. No.	Compounds	Colour	% metal Calc.	% metal Obs.	% Nitrogen Calc.	% Nitrogen Obs.	B.M.
1.	$Ni(PAS)_2.2H_2O$	Green	15.30	15.29	7.29	7.20	3.221
2.	$Ni(PAS)_2.Py_2.2H_2O$	Green	10.82	10.68	10.33	10.22	3.343
3.	$Ni(PAS)_2\ Pico_2.2H_2O$	Green	10.29	10.23	9.82	9.81	3.212
4.	$Ni(PAS).(Oxine).2H_2O$	Yellowish green	15.02	15.00	7.16	7.07	2.890
5.	$Ni(PAS)(Nico).2H_2O$	Light green	15.92	15.84	7.59	7.58	3.229

TABLE 2 - OBSERVED BAND POSITIONS FROM REFLECTANCE SPECTRA

Sl. No.		nm	cm^{-1}
1.	$Ni(PAS)_2.2H_2O$	320, 565, 690, 925	31250, 17699, 14493, 10811
2.	$Ni(PAS)_2.Py_2.2H_2O$	390, 610, 700	25641, 16377, 14285,
3.	$Ni(PAS)_2.Pico_2.2H_2O$	340, 480, 615, 690	29412, 20833, 16260, 14493
4.	$Ni(PAS).(Oxine).2H_2O$	390, 560, 660, 855	25641. 17857, 15151, 11696
5.	$Ni(PAS)(Nico).2H_2O$	330, 385, 580, 660	30303, 25974, 17241, 15151

TABLE 3—PRINCIPAL BANDPOSITIONS (cm^{-1}) WITH ASSIGNMENTS

S.No.	Compound	$^3A_{2g}\rightarrow{}^3T_{2g}$ (ν_1)	$^3A_{2g}\rightarrow{}^3T_{1g}$ (F) (ν_2)	$^3A_{2g}\rightarrow{}^3T_{1g}$ (P) (ν_3)	$\frac{\nu_3}{\nu_1}$	$\frac{\nu_2}{\nu_1}$	$\frac{\nu_3}{\nu_2}$
1.	Ni $(PAS)_2.2H_2O$	10811	17860	31250	2.892	1.653	—
2.	Ni $(PAS)_2.Py_2.2H_2O$	10640	16377	25643	—	1.535	1.566
3.	Ni $(PAS)_2.Pico_2.2H_2O$	9743	16260	29412	—	1.669	1.808
4.	Ni (PAS) (Oxine).$2H_2O$	11696	17857	27920	2.388	1.528	—
5.	Ni (PAS) (Nico).$2H_2O$	10420	17241	30303	—	1.635	1.758

TABLE 4—SPECTROCHEMICAL PARAMETERS

S. No.	Compound	10 Dq (cm^{-1})* aquo ion	10 Dq (cm^{-1}) complex	$\frac{Dq}{B}$	Bo (cm^{-1})† gaseous ion	B (cm^{-1}) complex	β
1.	Ni $(PAS)_2.2H_2O$	8500	10811	0.972	1080	1112	1.030
2.	Ni $(PAS)_2.Py_2.2H_2O$	8500	10640	1.600	1080	662	0.616
3.	Ni $(PAS)_2.Pico_2.2H_2O$	8500	9743	0.890	1080	1095	1.014
4.	Ni (PAS) (Oxine).$2H_2O$	8500	11696	1.639	1080	713	0.660
5.	Ni (PAS) (Nico).$2H_2O$	8500	10420	0.961	1080	1084	1.003

* C.S.G. PHILLIPS and R.J.P. WILLIAMS : "Inorganic Chemistry" Vol. 2 (Oxford).

† B.N. FIGGIS : "Introduction to Ligand Fields", (John Wiely and Sons).

Elmer I.R. spectrophotometer model 577 (4000 cm^{-1} to 200 cm^{-1}) by KBr disc technique.

Discussion

The perusal of Table 4 indicates that the mixed ligand complexes of Ni(II) taking para amino salicylic acid as primary ligand and pyridine, β-picoline as secondary ligands have the composition $NiL_2X_2.2H_2O$ where L is primary ligand and X the secondary ligand. In case of oxine and nicotinic acid as secondary ligand, the composition is $MLX.2H_2O$.

Ni(II) complexes with coordination number six are always high spin complexes with either regular or distorted octahedral stereochemistries. The ^3F Russel Saunders term splits into three components $^3A_{2g}$, $^3T_{2g}$ and $^3T_{1g}$ in order of increasing energy. Thus three spin allowed transitions are expected,

$$^3A_{2g}\rightarrow{}^3T_{2g} \qquad (\nu_1)$$

$$^3A_{2g}\rightarrow{}^3T_{1g}(F) \qquad (\nu_2)$$

and

$$^3A_{2g}\rightarrow{}^3T_{1g}(P) \qquad (\nu_3)$$

These three transitions are observed in the regions 7000-13000, 11000-20000 and 20000-28000 cm^{-1} respectively. As a result of this the 10 Dq values in octahedral Ni(II) complexes are seen to vary from 6800 to 12700 cm^{-1}. In addition to these three traisitions two spin forbidden transitions to ^1E_g and $^1T_{2g}$ are sometimes observed. Thus transition to spin singlet level, $^3A_{2g}\rightarrow{}^1E_g$, a band is observed in the region 11000-15000 cm^{-1} while a band in the region 17000-22000 cm^{-1} is assigned to $^3A_{2g}\rightarrow{}^1T_{2g}$ transition.

Band positions observed from the reflectance spectra of various complexes, studied in the present investigation, showed that in case of Ni (PAS $)_2.Py_2.2H_2O$, Ni (PAS $)_2.Pico_2.2H_2O$ and Ni (PAS) (Nico).$2H_2O$ the ν_1 band is not obseved, however their presence in near I.R. has been indicated by the upward trend of the corresponding reflectance spectra. Because of instrumental range we could not locate the exact position of this band and therefore the theoretical band assignment has been made as described by Lever[6]. Similarly in case af Ni$(PAS)_2.2H_2O$ the ν_2 band could not be assigned exactly and, therefore, here also the theoretical band assignment has been made as described by Lever[6]. The values of ν_1, ν_2, ν_3 corresponding to their transitions are given in Table 3. The ratio ν_2/ν_1, ranges between 1.53 to 1.67, which is characteristic of all the Ni(II) complexes having pseudo octahedral environments, suggesting thereby strong T_{1g} term interactions[7].

In cas of Ni$(PAS)_2.2H_2O$ and Ni$(PAS)_2.Py_2.2H_2O$ a weak shoulder is observed near about 14000 cm^{-1}. This is probably due to spin forbidden transition $^3A_{2g}\rightarrow{}^1E_g$ as suggested by Jorgensen[8]. All these results, therefore, show that all the Ni(II) complexes,

studied in the present investigation, possess octahedral stereochemistries. 10 Dq and B values are calculated, as suggested by Lever and are recorded in Table 4. These values are in very good agreement with those reported for octahedral Ni(II) complexes[7]. In addition to these two parameters the nephelauxatic coefficient, β, has also been calculated. Based on the values of β, the nephelauxatic series is as under :

$Ni(PAS)(Oxine).2H_2O > Ni(PAS)_2.Py_2.2H_2O >$

$Ni(PAS)_2.2H_2O > Ni(PAS)(Nico).2H_2O >$

$Ni(PAS)_2.Pico_2.2H_2O$.

The magnetic moments for all the Ni(II) complexes are recorded in Table 4. The perusal of Table 4 indicates that these values are in the range expected for Ni(II) octahedral complexes. The $^3A_{2g}$ ground term can generate no orbital contribution. However, spin orbit coupling mixes the first excited $^3T_{2g}$ term into the $^3A_{2g}$ term, the mixing in effect being expressed quantitatively as :

$$\mu=\mu_0\left(1-\frac{4\lambda}{10\,Dq}\right)$$

where μ_0 is the spin orbit coupling constant. Since λ is negative for Ni(II) complexes it follows that moment will be higher the lower the 10 Dq i.e. weaker the ligand is. The experimental magnetic moments lie usually within the range 2.9 to 3.3 B.M. ; they are independent of temperatures and of small departures of octahedral symmetry. In the present investigation magnetic moments of the complexes fall within the range 2.89 to 3.34 B. M. The observed deviation in magnetic moments from the spin only value could be due to second order Zeeman effects between the ground state and the highest ligand field terms.

I.R. spectra of the compounds show the characteristic bands of hydroxy acids and the secondary ligands. In case of oxine and nicotinic acid complexes the bands in the neighbourhood of 800 cm^{-1} confirm that the water molecule is present as coordinated water in accordance with Fujita et at[9]. In other cases the bands observed at about 600 cm^{-1} may be assigned for the presence of lattice water in accordance with Nakamoto[10]. In all cases M-O band is observed at about 400 cm^{-1}. The I.R. spectrum of pyridine shows the presence of characteristic bands of pyridine at 700, 598 and 400 cm^{-1}, the latter two are due to in plane and out of plane ring deformations respectively. Similarly, I.R. spectrum of β-picoline shows the presence of characteristic bands of β-picoline at 780, 700, 620 and 400 cm^{-1}.

In the high frequency region the pyridine vibrations show very little shift upon complex formation. However, those of in-plane and out-of-plane ring deformations are shifted to higher frequencies upon coordination to metal, and are observed at about 640 and 430 cm^{-1} respectively. The shifting of these bands to higher frequency region, therefore, confirms that pyridine and β-picoline, are coordinated to the metal ion. The M-P_y and M-Pico stretching vibrations occur near about 230 cm^{-1}. In all the mixed ligand complexes the observed band in the neighbourhood of 500 cm^{-1}, according to Nakamoto, may be regarded as the evidence of bonding of nitrogen to metal ion. Thus, the tertiary nitrogen of pyridine, β-picoline, 8-hydroxyquinoline and nicotinic acid is attached to the metal ion as a secondary ligand forming mixed ligand complexes in all cases.

References

1. G. C. Bhattacharya and P. C. Sinha, *J. Indian Chem. Soc.*, 1955, 32, 317, 414.
2. A. B. P. Lever, *Inorg. Chem.*, 1965, 4(5), 763.
3. D. C. Patel, R. C. Sharma and P. K. Bhattacharya, *J. Indian Chem. Soc.*, 1971, 48, 233.
4. P. V. Khadikar, R. L. Ameria, N. G. Kekre and S. D. Chauhan, *J. Inorg. Nuclear Chem.*, 1973, 35, 4301.
5. P. W. Selwood, "Magnetochemistry", Interscience Publishers (N. Y.) 1956, p. 6.
6. A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, 1968.
7. A. B. P. Lever, *Coord. Chem. Rev.*, 1968, 3, 119.
8. C. K. Jorgensen, *Acta. Chem. Scand.*, 1956, 10, 887.
9. J. Fujita, K. Nakamoto and M. Kobayaski, *J. Amer. Chem. Soc.*, 1956, 78, 3963.
10. K. Nakamoto, "Infra-red spectra of Inorganic and Coordination Compounds", Wiely - Interscience (N.Y.), 1970, p. 151, 167.

J. Indian Chem. Soc.,
Vol. LVII February 1980, pp. 116-119

Determination of Dissociation Constant (pK) and Stability Constant of Pb^{+2}, Cd^{+2}, UO_2^{+2} Complexes of Monosodium L-Glutamic Acid

R. S. SAXENA and G. L. KHANDELWAL

Department of Chemistry, Malaviya Regional Engineering College, Jaipur, India

Manuscript received 21 August 1979, accepted 30 November 1979

The dissociation constant (*p*K) of monosodium L-glutamic acid has been determined at a constant ionic strength $\mu = 0.1M$ ($NaClO_4$) in aqueous and in different 50% (V/V) solvents, viz., methanol, ethanol, isopropanol, acetonitrile, dimethyl formamide and various concentrations of dimethyl sulfoxide by potentiometric technique, adopting Albert and Serjeant method. The *p*K value of $-NH_2$ group has been found to increase with increase in viscosity and ionic interactions of the solutions.

The formation, composition and stability constants of the title metal ions with monosodium L-glutamic acid have been studied polarographically, adopting DeFord and Hume's method for Cd^{+2}, Pb^{+2} ions and Lingane method for UO_2^{+2} ion. The plot of $-E_{1/2}$ VS $-$log ligand showed the existence of 1:1 and 1:2 complex species for Cd^{+2}, Pb^{+2} ions and 1:1 complex species of UO_2^{+2} ion in aqueous solution at 25°. The overall stabilities of the complexes formed in aqueous solution are log K_c = 5.74, 4.15, 3.10 for Pb^{+2}, Cd^{+2} and UO_2^{+2} – monosodium L-glutamic acid respectively. The overall changes in free energy of the complexation reactions have also been determined.

AMINO acids containing an active $-NH_2$ and $-COOH$ group, are well known for their tendency to form complexes with metals and have great significance in biological, pharmaceutical fields and are directly involved in all the metabolic, enzymatic activities of every living being. Polarographic behaviour and metal complexes of several such amino acids or compounds have been nvestigated by various research workers[1-7]. This commiunication reports the formamion, composition and stability constants of lead, cadmium and uranyl complexes with monosodium L-glutamic acid. Dissociation constant (pK) of monosodium L-glutamic acid has also been determined in aqueous and in different 50%(V/V) solvents, viz., methanol, ethanol, isopropanol, acetonitrile, dimethyl formamide and in various concentrations of dimethyl sulfoxide by potentiometric technique, adopting Albert and Serjeant method.

Experimental

L-glutamic acid [$HOOC.CH_2.CH_2.CH(NH_2)COOH$] was biochem 'A grade' BDH poole, England and all other chemicals used were of AnalaR grade. L-glutamic acid as such is not soluble in aqueous medium hence its monosodium salt is prepared by dissolving calculated quantity of L-glutamic acid in a standard solution of NaOH (corresponding to monosodium salt). Fresh solution of metal salts were used to avoid the effects of ageing and oxidation (if any). All solutions used in polarographic measurements had in addition to monosodium glutamic acid, metal ion, $0.1M$ $NaClO_4$ and 0.002% Triton-X-100. The entire study was carried out in an atmosphere of nitrogen.

A manual polarograph with scalamp galvanometer as current recorder and S.C.E. as reference electrode have been used for recording the polarograms. The capillary used had the following characteristics in $0.1M$ $NaClO_4$ at -0.5V vs S.C.E. with h_{eff} value being 48.13 cm; m = 1.39 mg/sec; t=4.3 sec/drop in nitrogen atmosphere at 25°.

For determining the dissociation constant of monosodium L-glutamic acid, the calculated amount of monosodium L-glutamic acid corresponding to $0.01M$ per 50 ml solution in 50% solvent and $0.1M$ $NaClO_4$ (giving a total volume of 47.5 ml) is prepared. Then it was titrated against $0.1M$ NaOH in an inert atmosphere of nitrogen by adding the titrant in 10 equal portions, each a tenth of an equivalent, and *p*H was recorded as equilibrium reached after each addition.

All *p*H – measurements were made on a Cambridge benchpattern *p*H meter (accuracy ± 0.02 *p*H unit) with glass calomel electrode assembly and temperature of the cell was maintained by a thermostat (U_8 – type, German) having an accuracy of $\pm 0.1°$. Requisite quantities of $NaClO_4$ were added to the solution for maintaining constant ionic strength ($\mu = 0.1M$).

Results and Discussion

Dissociation constant:

L-glutamic acid as such is not soluble in aqueous medium, hence its monosodium salt is prepared which

exists in the form of 'Zwitterion' and may be represented as[8,9]

$$NaOOC-CH_2-CH_2-CH\,(^{+}NH_3)-COO^{-} \quad \ldots (I)$$

The dissociation constant of monobasic acid, (I), may be determined by the following mechanism

$$NaOOC-CH_2-CH_2-CH(^{+}NH_3)-COO^{-} \rightleftharpoons$$

$$NaOOC-CH_2-CH_2-CH(NH_2)-COO^{-}+H^{+} \quad \ldots (1)$$

By law of mass action:

$$K=\frac{[H^{+}][NaOOC-CH_2-CH_2-CH(NH_2)-COO^{-}]}{[NaOOC-CH_2-CH_2-CH(^{+}NH_3)\,COO^{-}]} \quad \ldots (2)$$

In dilute solutions, the concentration may be taken as equivalent to activities. Equation (2) may be written as

$$pK=pH+\log\frac{[NaOOC-CH_2-CH_2-CH(^{+}NH_3)-COO^{-}]}{[NaOOC-CH_2-CH_2-CH(NH_2)-COO^{-}]} \quad \ldots (3)$$

Hence, for determination of pK value of monosodium L-glutamic acid, the ratio

$$\frac{[NaOOC-CH_2-CH_2-CH(^{+}NH_3)-COO^{-}]}{[NaOOC-CH_2-CH_2-CH-(NH_2)\,COO^{-}]}$$

should be known at a particular pH, and this ratio may be determined from the stoichiometric concentrations, i.e. those concentrations which would be present if each portion of the alkali reacted with its equivalent of monosodium L-glutamic acid. Expression (3) may be written as follows for the correction of hydroxyl ion concentration.

$$pK=pH+\log\frac{[NaOOC-CH_2-CH_2-CH(^{+}NH_3)-COO^{-}]+[OH^{-}]}{[NaOOC-CH_2-CH_2-CH(NH_2)-COO^{-}]-[OH^{-}]} \quad \ldots (4)$$

The pK value of $-NH_2$ group of monosodium L-glutamic acid in 50% (V/V) different solvents are determined at 25°, which show the following order [Table 1].

DMSO > DMF > Acetonitrile > Isopropanol > Ethanol > Methanol

This may be partly due to change in dielectric constant[10] of the medium which depends on the viscosity and ionic interactions of the solution[11].

The pK value in aqueous and in various concentration of DMSO has also been determined [Table 1].

TABLE 1—VALUES OF DISSOCIATION CONSTANT (pK) OF $-NH_2$ GROUP OF MONOSODIUM L-GLUTAMIC ACID (0.01M) AT IONIC STRENGTHS μ=0.1M ($NaClO_4$) IN DIFFERENT PERCENTAGES (V/V) OF NON-AQUEOUS MEDIUM AT 25°C.

Sl. No.	Medium	pK-value
1.	Aqueous (100%)	9.56
2.	Methanol (50%)	9.75
3.	Ethanol (50%)	9.77
4.	Isopropanol (50%)	9.80
5.	Acetonitrile (50%)	9.82
6.	Dimethyl formamide (50%)	10.14
7.	Dimethyl sulfoxide (50%)	10.33
8.	Dimethyl sulfoxide (40%)	10.13
9.	Dimethyl sulfoxide (30%)	9.94
10.	Dimethyl sulfoxide (20%)	9.76
11.	Dimethyl sulfoxide (10%)	9.64

Lead and Cadmium-Monosodium L-Glutamic Acid System :

Both lead and cadmium-monosodium L-glutamic acid complexes at d.m.e. give a well defined cathodic wave in aqueous medium. The reduction is found to be diffusion controlled[12], two electron reversible step for both the systems as is evident from the constant value of $i_d h_{eff}^{1/2}$ (Fig. 1) within experimental conditions and from the plots of $\log i/i_d-i)$ vs $-E_{d.e.}$, whose values of slopes (0.03±0.003) V, were agreeing with the theoretical value of 0.03V of two electron transfer process[13].

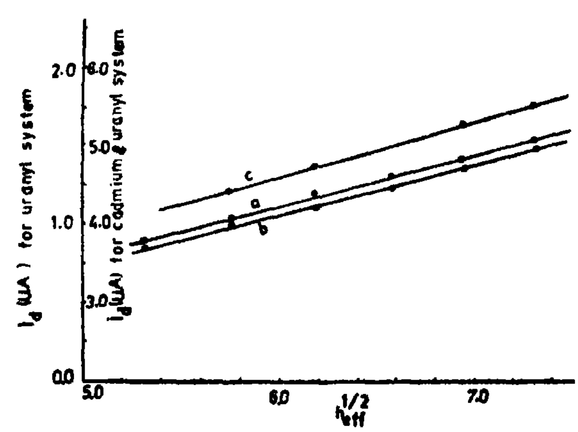


Fig. 1. Plot of i_d vs $h_{eff}^{1/2}$ for
(a) Cd^{+2} - monosodium L-glutamic acid system
(b) Pb^{+2} - monosodium L-glutamic acid system
(c) UO_2^{+2} - monosodium L-glutamic acid system

Effect of varying [ligand] :

The cathodic shift in $E_{1/2}$ coupled with decrease in diffusion current on increasing [ligand] 0.000*M* to 0.012 *M* [Table 2 for Cd^{+2} system and Table 3 for Pb^{+2} – system] shows the formation of complex species. The curvature obtained in the plot of $-E_{1/2}$ vs – log [ligand] of both the systems showed the formation of successive complexes.

TABLE 2 – VALUES OF $E_{1/2}$, i_d AND VARIOUS FUNCTIONS FOR Cd^{+2}-MONOSODIUM L-GLUTAMIC ACID SYSTEM AT 25°C

Sl. No.	Concn. of ligand C_X (M)	$-E_{1/2}$ (Volts)	i_d (μA)	$F_0(X)$	$F_1(X)$	$F_2(X)$
1.	0.000	0.5890	5.47	—	—	—
2.	0.016	0.5920	5.28	1.3094	19.3375	—
3.	0.024	0.5980	5.18	2.1314	47.1417	380.90
4.	0.040	0.6030	5.03	3.2419	56.0475	—
5.	0.056	0.6062	4.88	4.2898	58.7464	370.47
6.	0.080	0.6110	4.80	6.3415	66.7688	359.61
7.	0.120	0.6177	4.75	10.8100	81.7500	364.58

TABLE 3 – VALUES OF $E_{1/2}$, i_d AND VARIOUS FUNCTIONS FOR Pb^{+2}-MONOSODIUM L-GLUTAMIC ACID SYSTEM AT 25°C

Sl. No.	Concn. of ligand C_X (M)	$-E_{1/2}$ (Volts)	i_d (μA)	$F_0(X)$	$F_1(X)$	$F_2(X)$
1.	0.00	0.3950	6.05	---	—	—
2.	0.01	0.4062	5.35	2.7097	170.97	3597
3.	0.02	0.4145	5.17	5.3589	217.94	4147
4.	0.04	0.4242	4.97	11.8815	272.04	3426
5.	0.06	0.4327	4.85	23.6321	377.20	4036
6.	0.08	0.4375	4.70	35.4613	430.76	3697
7.	0.10	0.4430	4.66	54.9450	539.75	4044

Calculation of overall stability constants :

According to DeFord and Hume's method[14]

$$F_0(X) = \text{antilog}\left\{0.435\frac{nF}{RT}\left[(E_{1/2})_S - (E_{1/2})_C\right] + \log\frac{I_S}{I_C}\right\} \quad (1)$$

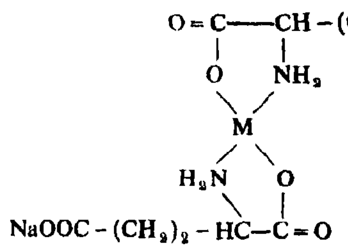
Herewith the sign and meaning of the terms are the same as those in[15], which became conventional. The complexity function $F_j(X)$ is defined as

$$F_j(X) = 1 + \beta_1(X) + \beta_2(X)^2 + \dots\beta_n(X)^n + \dots\beta_N(X)^N \quad \dots(2)$$

where (X) is the ligand concentration (C_x), n is the number of ligand molecules ; ($O \leq n \leq N$). N is the co-ordination number of the complex forming, metal (M) and β_n is the overall stability constant of the complex, MX_n. From the experimental data, the complexity function F_j (X) which is polynomial in (X), is set up ; the coefficient of the latter are required, β_n. Graphical extrapolation reduces the polynomial equation (2) to N-equations from which the corresponding β_n are obtained and are given below :

Composition of complex	*log stability values at 25°C*	
	Pb^{+2} – system	Cd^{+2} – system
1 : 1	2.13	1.58
1 : 2	3.61	2.57

Probably five membered ring is formed between lead and cadmium ions with monosodium L-glutamic acid[16].



where M stands for Pb^{+2} and Cd^{+2}.

From the known stability constant data, values of degree of formation α_j for each complex in a system have been calculated from the following equation[18] at 25°.

$$\alpha_j = \frac{\beta_j(X)^j}{F_0(X)} \quad \dots \quad (3)$$

Uranyl -Monosodium L-Glutamic Acid System :

Uranyl-monosodium L-glutamic acid complex at d.m.e. gives a well defined cathodic wave in aqueous medium. Reduction is found to be diffusion controlled one electron reversible step as is evident from the constant value of $i_d/h_{eff}^{1/2}$ (Fig. 1), within experimental conditions and from the values of $E_{3/4} - E_{1/4}$ which were (0.06 ± 0.006)V agreeing with the theoretical value of one electron transfer process[18].

Effect af varying [ligand] :

The cathodic shift in $E_{1/2}$ coupled with decrease in diffusion current (i_d) on increasing [ligand] 0.000*M* to 0.016*M* (Fig. 1) shows the formation of complex species. The plot of $-E_{1/2}$ vs – log [ligand] result in a straight line, hence the complex formed consists of only one species. The number of ligands/metal ion i.e. p. has been determined from the slope of the plots of $-E_{1/2}$ VS – log [ligand] at temperature 25° and is 0.88≃1.0.

Formation of complex species between UO_2^{+2} and monosodium L-glutamic acid may be explained as five membered ring[17].

Determination of stability constant :

According to Lingane method

$$(E_{1/2})_C - (E_{1/2})_S = \frac{0.0591}{n} \log K_C - p.\frac{0.0591}{n} \log C_X \quad ...(4)$$

Here the sign and meaning of the terms are same as those in [18] which became conventional.

From equation (4) using experimental data, stability constant is determined from the extrapolation at $-\log C_X$ or log [ligand] = 0 and is found to be 3.10.

The overall changes in free energy ($\triangle G$) of the complexation reactions follows the order :

Pb^{+2} – system > Cd^{+2} – system > UO_2^{+2} – system
– 1.04 K.cal/mole – 0.85 K.cal/mole – 0.67 K.cal/mole.

References

1. V. H. DAYAN, *Diss. Abstr.*, 1954, **14**, 1906.
2. Y. OKAZAKI and T. OTSUKI, *Rev. Polarogr.*, (Kyoto); 1967, 14(3-6), 307.
3. T. R. KOCH and W. C. PURDY, *Anal. Chim. Acta.*, 1971, 54, 271.
4. R. S. SAXENA and G. L. KHANDELWAL, *Indian J. Chem.*, 1977, 15A, 757.
5. A. GERGELY and J. MOJZES, *J. Inorg. Nuclear Chem.*, 1972, 34(4), 1277.
6. JOHN B. LETTER JR. and E. BAUMAN JOHN JR., *J. Amer. Chem. Soc.*, 1970, 92(3), 437.
7. N. C. LI, B. DOODY and J. M. WHITE, *J. Amer. Chem. Soc.*, 1958, 80, 5901.
8. E. Q. ADAMS, *J. Amer. Chem. Soc.*, 1916, 38, 1503.
9. E. CONN and P. K. STUMPF, 'Outlines of Biochemistry', John Wiley, New York, 1965.
10. M. C. DAY and J. SELBIN, 'Theoretical Inorganic Chemistry', Reinhold Pub. Corporation, New York, 1966.
11. N. F. HALL and M. R. SPRINKLE, *J. Amer. Chem. Soc.*, 1932, 54, 3469.
12. L. MEITES, 'Polarographic Tehniques', Interscience Pub., New York, 1965.
13. D. R CROW, 'Polarography of Metal Complexes', Academic Press, London, 1969.
14. D. D. DEFORD and D. N. HUME, *J. Amer. Chem. Soc.*, 1951, 73, 5221.
15. D. D. DEFORD, D. N. HUME and G. C. CAVE, *J. Amer. Chem. Soc.*, 1951, 73, 5223.
16. N. C. LI and E. DOODY, *J. Amer. Chem. Soc.*, 1952, 74, 4184.
17. I. FELDMAN and L. KOVAL, *Inorg. Chem.*, 1963, 2, 145.
18. J. J. LINGANE, *Chem. Rev.*, 1941, 29, 1.

J. Indian Chem. Soc.,
Vol. LVII, February 1980, pp. 120-123

Studies on the Coordination of Pyridine and β-Picoline with *Bis*-(2-hydroxyacetophenone oximato) and *Bis*-(2-hydroxy-5-methylacetophenone oximato) nickel(II)

M. S. PATIL, R. P. PATEL and J. R. SHAH

Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar-388 120, Gujarat

Manuscript received 21 August 1979, accepted 20 December 1979

Adducts of bis-(2-hydroxyacetophenone oximato) nickel(II) and bis-(2-hydroxy-5-methylacetophenone oximato)-nickel(II) with pyridine and β-picoline having general formula NiL_2L_2' have been prepared and they are characterized by their electronic spectral and magnetic properties. The ligand-field and nephelauxetic parameters evaluated from the spectra using ligand-field theory of spin-allowed transitions are found consistent with six-coordinate structure for these adducts.

It is observed that diamagnetic, square-coordinated complexes of Ni(II) develope paramagnetism when they are dissolved in various organic solvents[1]. This behaviour of the Ni(II) complexes was attributed to the equilibrium between square and tetrahedral forms of the complexes. It is also well-known that diamagnetic, square-coordinated Ni(II) has a strong tendency to increase its coordination number by interaction with additional ligands at right angles to the plane of the parent molecule. By this way the resulting complex is found to have octahedral structure and paramagnetic behaviour[2,3]. The present work describes the preparation of such paramagnetic Ni(II) complexes. These NiL_2L_2' complexes have been prepared by mixing the solutions of 4-coordinated Ni(II) complexes of 2-hydroxyacetophenone oxime (HAO) and 2-hydroxy-5-methylacetophenone oxime (MHAO) NiL_2 with pyridine and β-picoline, L'.

Experimental

HAO (M.P. 116°C) and MHAO (M.P. 143°C) were prepared by the aqueous ethanolic alkali method and were recrystallized from ethanol. All chemicals used were of reagent grade. $Ni(HAO)_2$ and $Ni(MHAO)_2$ were prepared using the literature method[4,5]. The adducts of the above complexes with pyridine and β-picoline were prepared as follows. First, the NiL_2 was dissolved in the base L' and warmed for some time on a water bath. The resulting solution was cooled and then petroleum ether was added to it to precipitate the adduct which was filtered, washed with ether and dried by suction. The solid adducts are found to be unstable, showing a tendency to give up the base and form the original compound. For establishing the composition, metal content in each adduct was determined by independent gravimetric and volumetric methods. As the adducts are unstable, the amount of base was determined by heating the adducts to constant weight in an oven at 80°. The metal contents of the residues obtained as above correspond to that of the parent complex, NiL_2, the residue also shows diamagnetic behaviour. These observations establish the identity of the residues with parent compounds.

A "Sartorius" semi-micro Gouy-balance was used to determine the magnetic susceptibilities of the complexes. The gouy tube was calibrated using $[Hg\ Co(NCS)_4]$[6]. The diffuse reflectance electronic and solution electronic spectral measurements were made on Beckmann DU spectrophotometer. The solutions for spectral measurements were made by dissolving the parent complex in adequate quantity of appropriate base to prevent dissociation of base from the adduct and then diluting with benzene.

Results and Discussion

Analytical data (Table 1) reveal 1:2 (metal : ligand) stoichiometry for the parent complexes and 1 : 2 : 2 (metal : ligand : base) stoichiometry for the adducts.

The diffuse reflectance and solution electronic spectral data are given in Table 1 and 2 respectively. The magnetic moments of the complexes are included in Table 1. It can be seen that the parent complexes NiL_2 must have a square planar structure, as they exhibit a strong characteristic band around 16, 660 cm^{-1} [7]. Diamagnetic behaviour of these complexes also support the planar structure. The solution spectral data for the adducts consistent with an octahedral structure. Thus all the adducts show three bands in their normally expected regions for Ni(II) octahedral complexes. The spectra are quite similar to those of the complexes of the type $NiL_4X_2^8$.

Assuming an average effect from the ligand atoms[9,10] it is possible to use the energy levels for d^8 configuration in octahedral field. The following three spin allowed transitions are possible.

$$\nu_1 : {}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F) \quad \ldots \quad (1)$$

$$\nu_2 : {}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F) \quad \ldots \quad (2)$$

$$\nu_3 : {}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P) \quad \ldots \quad (3)$$

According to the weak field approximation the energy of the first band ν_1, corresponds to *10Dq*. While the second and third transitions are mixed by configuration interaction and their energies can be determined by

$$\nu_{2,3} = \frac{1}{2}(15B + 30Dq) \mp \frac{1}{2}[(15B - 10Dq)^2 + 120Dq]^{1/2} \quad \ldots \quad (4)$$

The interelectronic repulsion parameter, B, was obtained using the following different equations[11].

$$\text{(a)} \quad B = \frac{2\nu_1^2 + \nu_2^2 - 3\nu_1\nu_2}{(15\nu_2 - 27\nu_1)} \quad \ldots \quad (5)$$

$$\text{(b)} \quad B = \frac{\nu_2 + \nu_3 - 3\nu_1}{15} \quad \ldots \quad (6)$$

$$\text{(c)} \quad B = \frac{1}{75}[3\nu_1 \pm \{25(\nu_3 - \nu_2)^2 - 16\nu_1^2\}^{1/2}] \quad \ldots \quad (7)$$

From the following equations we have calculated both B and 10Dq using ν_2 and ν_3.

$$\text{(d)} \quad 10Dq = \frac{1}{34}[9(\nu_2 + \nu_3) \pm \{81(\nu_2^2 + \nu_3^2) - 178\,\nu_2\nu_3\}^{1/2}] \ldots (8)$$

$$B = \frac{\nu_2 + \nu_3 - 30Dq}{15} \quad \ldots \quad (9)$$

$$\text{(e)} \quad B = \frac{1}{510}[7(\nu_2 + \nu_3) \pm \{49(\nu_2 + \nu_3)^2 + 680(\nu_3 - \nu_2)^2\}^{1/2}] \ldots (10)$$

$$10Dq = \frac{1}{3}(\nu_2 + \nu_3) - 5B \quad \ldots \quad (11)$$

Because of instrumental limitations of measurements it was not possible to obtain the ν_3 band. However, we do observe strong intense tail in the region 25000 cm^{-1}. This may allow us to conclude that, the spin allowed transition, ν_3, would exist in the range where our complexes exhibit strong charge transfer absorptions. Therefore, we have used eq. (5) to calculate then B and using this B and observed ν_1 = 10Dq, we have calculated ν_3 by eq. (4). This calculated ν_3 along with observed ν_1 and ν_2 were used to calculate B_{35} by equations (6) and (7). After getting 10Dq and B, equation (4) was used to get ν_2 and ν_3. The values, thus obtained are given in Table 2. Examination of Tables 1 and 2 suggests the following.

(i) The difference in the chemical nature of the ligands has little effect on the 10Dq values. It means, that atoms beyond the first coordination sphere have only a small influence on the absorption spectrum[10,12].

(ii) The appearance of ν_1 band in the spectra shows some signs of splitting, suggesting that it is not possible to consider that an average effect from the ligand atoms determines the spectral shape. Infact, in Oh symmetry it is not possible to find any splitting of the ν_1 band. However, in lower symmetry, D_{4h}, ν_1 frequently splits. These are assigned as transitions to the ${}^3B_{2g}$ and ${}^3E_g$ (components of ${}^3T_{2g}$) levels. Thus the structure in the ν_1 band may be assigned to the lowering of symmetry in the adducts.

(iii) For all the systems, the transition energy, ν_3, is calculated and this was fitted for other methods. From the table it appears that, the calculated energies are very close to the observed energies. Band fittings by method (e) give rather larger $\delta\nu$ in all the systems studied. Therefore, it may be concluded that this may not be a better method.

(iv) The ratio ν_2/ν_1 of the frequencies of the first and second band maxima lies in the range required for octahedral complexes of nickel (II)[13].

(v) All the complexes have magnetic moments in the range 3.1 to 3.3 and thus confirm the octahedral coordination around Ni(II). In an attempt to correlate the spectral and magnetic data, μ_{eff} were calculated using 10Dq = ν_1 and λ_0 = −315 by

$$(\mu_{eff})_{cal.} = \mu_{eff}^{s.o.}\left(1 - \frac{4\lambda_0}{10Dq}\right) \quad \ldots \quad (12)$$

The calculated values (Table 1) are found to be in good agreement with the observed values, indicating small orbital contribution because of the spin-orbit coupling between the first excited state ${}^3T_{2g}$ and ground state. This also suggests the validity of the ligand field parameter 10Dq, electron-electron repulsion parameter, B and the observed μ_{eff}.

(vi) ν_1 bands in the diffuse reflectance spectra of the adducts were observed as very broad bands. We also feel that the compounds would have probably decomposed during the measurements, and therefore, it is rather difficult to attach any significance to it.

TABLE 1—ANALYTICAL, SPECTRAL AND MAGNETIC DATA

Compound	% Base L' Found (Cal.)	% Nickel Found (Cal.)	Magnetic moment B.M. Found (Cal.)	Solution Spectral bands (Cm^{-1})	Diffuse Reflectance spectral band (Cm^{-1})
1. Ni(II) (HAO)$_2$	—	16.6 (16.36)	Diamagnetic	16660	15850
2. Ni(II) (HAO)$_2$ (β-picoline)$_2$	34.95 (34.48)	11.25 (10.93)	3.23 (3.17)	11100, 18180	11750 19610
3. Ni(II) (HAO)$_2$ (PY)$_2$	28.46 (30)	12.15 (11.78)	3.10 (3.17)	11180, 18180	11750, 19610
4. Ni(II) (MHAO)$_2$	—	15.55 (15.23)	Diamagnetic	16660	16130
5. Ni(II) (MHAO)$_2$ (β-picoline)$_2$	32.36 (33)	10.48 (10.26)	3.15 (3.17)	11140, 18180	11750, 19610
6. Ni(II) (MHAO)$_2$ (PY)$_2$	28.97 (28.43)	11.05 (10.83)	3.17 (3.17)	11100, 18180	—

TABLE 2—OBSERVED AND CALCULATED TRANSITION ENERGIES IN cm^{-1}

Compound	Method	ν_1	ν_2	ν_3	β_{15}	$\delta\nu_1$	β_{35}	ν_2/ν_1
	Expt.	11100	18180	—				1.64
	(a)	10 Dq	fitted	30905	1052		0.97	
Ni(HAO)$_2$	(b)	10 Dq	18180	30905	1052	± 0	0.97	
(β-picoline)$_2$	(c)	10 Dq	18170	30915	1050	± 10	0.97	
	(d)	11140	fitted	fitted	1044	± 40	0.97	
	(e)	12117	fitted	fitted	849	±1007	0.79	
	Expt.	11180	18180	—				1.63
	(a)	10 Dq	fitted	30365	1000		0.93	
Ni(HAO)$_2$	(b)	10 Dq	18180	30365	1000	± 0	0.93	
(PY)$_2$	(c)	10 Dq	18165	30380	998	± 15	0.92	
	(d)	11190	fitted	fitted	1005	± 10	0.93	
	(e)	11671	fitted	fitted	902	± 491	0.85	
	Expt.	18100	18180	—				1.64
	(a)	10 Dq	fitted	30905	1052		0.97	
Ni(MHAO)$_2$	(b)	10 Dq	18180	30905	1052	± 0	0.97	
(PY)$_2$	(c)	10 Dq	18170	30915	1050	± 10	0.97	
	(d)	11140	fitted	fitted	1044	± 40	0.97	
	(e)	12117	fitted	fitted	849	±1007	0.79	
	Expt.	11140	18180	—				1.63
	(a)	10 Dq	fitted	30560	1020		0.94	
Ni(MHAO)$_2$	(b)	10 Dq	18160	30560	1020	± 0	0.94	
(β-picoline)$_2$	(c)	10 Dq	18160	30580	1016	± 20	0.94	
	(d)	11160	fitted	fitted	1024	± 20	0.94	
	(e)	11867	fitted	fitted	902	± 727	0.86	

References

1. J. B. WILLS and D. P. MELLOR, *J. Amer. Chem. Soc.*, 1947, 69, 1237.
2. C. M. HARRIS, S. L. LENZER and R. L. MARTIN, *Aust. J. Chem.*, 1958, 11, 331.
3. T. S. KANNAN and A. CHAKRAVORTY, *Inorg. Chem.*, 1970, 9, 1153.
4. S. N. PODDAR, *Z. Anal. Chem.*, 1957, 154, 254.
5. H. SINGH and K. C. SHARMA, *Indian J. Appl. Chem.*, 1965, 28, 43.
6. B. N. FIGGIS and R. S. NYHOLM, *J. Chem. Soc.*, 1958, 4190.
7. R. S. NYHOLM, *Khim.*, 1956, 25, 329.
8. N. A. PATEL, J. R. SHAH and R. P. PATEL, *Indian J. Chem.*, (Communicated).
9. R. W. AMUNDSEN and O. BOSTRURO, *Acta. Ghem. Scand.*, 1957, 11, 1097.
10. O. BOSTRORO and C. K. JORGENSEN, *Acta. Chem. Scand.*, 1957, 11, 1223.
11. E. KONIG, Structure and Bonding, Springer—Verlag Berlin Heidelberg, New York, 1971, 9.
12. N. Z. BJERRUM, *Anorg. allg. Chem.*, 1909, 63, 140.
13. L. S. SACCONI, Transition Metal Chemistry, Marcel Dekker, Inc., New York, 1968, 4, 211.

J. Indian Chem. Soc.,
Vol. LVII, February 1980, pp. 124-126

Preparation of Salicylato and Nitrosalicylato Derivatives of Bis-π-Cyclopentadienyl Molybdenum(VI)-Oxo Dichloride and Bis-π-Indenyl Molybdenum(VI)-Oxo Dichloride

K. C. GOYAL and B. D. KHOSLA

Department of Chemistry, University of Delhi, Delhi-110 007

Manuscript received 5 July 1979, accepted 20 December 1979

The salicylato and nitrosalicylato derivatives of (I) bis-π-cyclopentadienyl molybdenum (VI)-oxo dichloride and (II) bis-π-indenyl molybdenum (VI)-oxo dichloride were obtained by heating salicylic or nitrosalicylic acid with (I) or (II) in benzene solution. They were found to react with only one mole of the salicylic or the nitrosalicylic acid. The products have been characterised by i. r. spectra.

A large number of derivatives of salicylic acid with metal halides have been reported which fall into three categories of derivatives : (a) Those in which only phenolic hydrogen is replaced, the carboxylic group remaining intact, for example reactions with Ti(IV)[1], Sn(IV)[2] and Fe(III)[3] halides. (b) Those in which the carboxylic group hydrogen is replaced, the phenolic group remaining intact, for example reactions with Ti(IV), Zr(IV), Th(IV) and Si(IV)[4] halides. (c) Those in which both the phenolic as well as carboxylic group hydrogen atoms have been replaced, for example reactions with W(VI)[5], WO(IV)[6] and Ce(III)[7] halides. These have been termed as 'salicylato' derivatives by Barbieri.[8] However there is no mention in literature of any reaction between salicylic acid and π-metallocene dihalides. The present communication describes the preparation of 'salicylato' and 'nitrosalicylato' derivatives of bis-π-cyclopentadienyl molybdenum-oxo dichloride and bis-π-indenyl molybdenum-oxo dichloride.

These derivatives have been prepared by refluxing the above named compounds with salicylic acid (or nitrosalicylic acids) in benzene until the evolution of hydrogen chloride ceased. Two mole ratios (1 : 1 and 1 : 2) were tried but it was found that one molecule of the molybdenum-oxo dichloride reacted with only one molecule of salicylic acid (or a nitrosalicylic acid). Analytical data and physical characteristics of the above derivatives are given in Table 1. These compounds are either dark violet or almost black in colour and are stable under dry conditions. The derivatives are non-volatile ; they do not sublime even in vacuum. They are sparingly soluble in benzene, dioxane, THF and are almost insoluble in petroleum ether and diethyl ether.

Experimental

Special precautions were taken to exclude moisture and all operations were carried out under anhydrous conditions. Benzene was dried over sodium metal. Bis-π-cyclopentadienyl molybdenum(VI)-oxo dichloride and bis-π-indenyl molybdenum(VI)-oxo dichloride were prepared by the method reported earlier.[9,10] 3-nitro, 5-nitro and 3,5-dinitrosalicylic acids[11-13] were prepared from salicylic acid by standard methods. Infrared spectra (in KBr) were recorded on Perkin-Elmer Infracord Model-137, spectrophotometer. Molybdenum was estimated as 8-hydroxyquinolate. Carbon, hydrogen and nitrogen were determined by the combustion method.

Preparation of salicylato derivatives of bis-π-cyclopentadienyl molybdenum(VI)-oxo dichloride

To 1.047 g (0.0033 mole) of bis-π-cyclopentadienyl molybdenum-oxo dichloride in 125 ml dry benzene was added 0.461 g (0.0033 mole) salicylic acid and the reaction mixture was refluxed. Evolution of hydrogen chloride began after half an hour and the contents gradually turned dark violet. The refluxing was continued until the evolution of hydrogen chloride ceased. The resulting mixture was then evaporated to dryness. On washing the residue with petroleum ether a dark violet coloured crystalline compound was obtained.

A similar procedure was adopted for the preparation of 3-nitro, 5-nitro and 3,5-dinitrosalicylato derivatives of bis-π-cyclopentadienyl molybdenum-oxo dichloride and salicylato, 3-nitro, 5-nitro and 3,5-dinitrosalicylato derivatives of bis-π-indenyl molybdenum-oxo dichloride.

TABLE 1 — DETAILS OF PREPARATION AND PROPERTIES OF SALICYLATO AND NITROSALICYLATO DERIVATIVES OF $(C_5H_5)_2MoOCl_2$ AND $(C_9H_7)_2MoOCl_2$

Compound	$(C_5H_5)_2MoOCl_2$ taken (g)	Amount of corresponding salicylic acid taken (g)	Colour of the compound	Analytical data: Metal Found	Metal Calcd.	Carbon Found	Carbon Calcd.	Hydrogen Found	Hydrogen Calcd.	Nitrogen Found	Nitrogen Calcd.
$(\pi\text{-}C_5H_5)_2MoO(C_7H_4O_3)$	1.047	0.461	dark violet	25.3	25.39	53.6	53.9	3.4	3.7		
$(\pi\text{-}C_5H_5)_2MoO(C_7H_3O_5N)$ 3–	0.877	0.512	-do-	22.4	22.69	47.8	48.2	3.1	3.07	3.1	3.3
$(\pi\text{-}C_5H_5)_2MoO(C_7H_3O_5N)$ 5–	0.908	0.531	blackish violet	22.3	22.69	48.0	48.2	3.0	3.07	3.12	3.3
$(\pi\text{-}C_5H_5)_2MoO(C_7H_2O_7N_2)$ 3,5–	0.626	0.456	blackish violet	20.4	20.5	43.2	43.5	2.4	2.56	5.78	5.98
	$(C_9H_7)_2MoOCl_2$ taken (g)										
$(\pi\text{-}C_9H_7)_2MoO(C_7H_4O_3)$	1.0325	0.345	blackish violet	20.1	20.08	62.4	62.8	3.5	3.76	—	
$(\pi\text{-}C_9H_7)_2MoO(C_7H_3O_5N)$ 3–	1.181	0.5233	-do-	18.13	18.3	56.98	57.3	3.0	3.2	2.5	2.67
$(\pi\text{-}C_9H_7)_2MoO(C_7H_3O_5N)$ 5–	0.9581	0.4245	Black	18.06	18.3	57.1	57.3	3.1	3.2	2.49	2.67
$(\pi\text{-}C_9H_7)_2MoO(C_7H_2O_7N_2)$ 3,5	0.6195	0.342	Black	16.68	16.9	52.67	52.8	2.63	2.8	4.73	4.9
	$MoOCl_4$ taken (g)									chlorine	
$MoOCl_2(C_7H_4O_3)$	0.7569	0.412	Black	29.8	30.0	26.1	26.3	1.0	1.2	22.0	22.2
$MoO(C_7H_4O_3)_2$	0.6807	0.7397	Violet black	24.8	25.00	43.55	43.7	2.0	2.08	——	

Results and Discussion

The compositions, as derived from elemental analysis of the various salicylato derivatives, suggest that one molecule each of $(C_5H_5)_2MoOCl_2$ or $(C_9H_7)_2MoOCl_2$ reacts with one molecule of salicylic acid (or nitrosalicylic acid), and both the chlorine atoms of molybdenum-oxo dichlorides are replaced by a salicylato group or a nitrosalicylato group. The chlorine atoms are eliminated as hydrogen chloride. The formation of the derivatives may be represented by the following general equation :

$$R_2MoOCl_2 + H_2A \longrightarrow R_2MoOA + 2\ HCl$$

where H_2A = salicylic or nitrosalicylic acid, one hydrogen being from the -COOH group and the other from the -OH group. R=cyclopentadienyl or indenyl group.

I.R. spectra of the salicylato derivatives

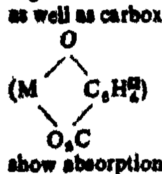
The infrared spectra of the various salicylato derivatives were recorded in the region 4000-670 cm^{-1}. The presence of $C_5H_5^-$ ring in these compounds is inferred by the i.r. absorption bands at $\sim$3000 cm^{-1} (C-H stretching), at 1150 cm^{-1} and 1030 cm^{-1} (C-H in-plane deformation) and at 860-840 cm^{-1} (C-H out-of-plane deformation). Sharp and strong absorption bands in the range 1460-1440 cm^{-1} indicate the C-C stretching (asymmetric ring breathing), and also the π-bonding of the ring with the molybdenum-oxo group.

The presence of indenyl group is indicated by the usual peaks due to $C_5H_5^-$ ring. The absorption bands due to phenyl part of the indenyl group appeared at 1610 cm^{-1} and 1450 cm^{-1} (C-C stretching), at $\sim$1380 cm^{-1} and $\sim$750 cm^{-1} (C-H in-plane and out-of-plane deformations respectively). A band at 710 cm^{-1} may be due to the methylene rocking vibration (since indene itself shows an absorption band at $\sim$700 cm^{-1}).

Metal carboxylate complexes show characteristic absorption bands in the region $\sim$1580 cm^{-1} (asymmetric -O-C-O-stretching) and at $\sim$ 1400 cm^{-1} (symmetric stretching of carboxylate group)[14]. Another group of strong absorption bands in the region 1040-1010 cm^{-1} and 825-700 cm^{-1} have been considered to be due to the metal-carboxylate linkage[15]. In cyclopentadienyl

and indenyl metal-phenoxy derivatives, the i.r. bands in the region ~ 1480 cm^{-1} have been attributed to the metal-phenoxy linkage.[16]

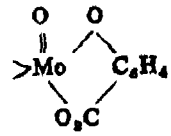
In these salicylato and nitrosalicylato derivatives where the molybdenum-oxo group is bonded to phenoxy as well as carboxylato groups, the i.r. spectra show a variation in the observed frequencies of metal-phenoxy and metal-carboxylato linkages. A. K. Babko et al.,[17] have inferred that metal salicylates containing a free phenolic group (M-O OC-C_6H_4OH) absorb in the region 1357-1310 cm^{-1}. while those in which the phenolic as well as carboxylic group hydrogens have been replaced



lack this absorption characteristic but show absorption bands in the *region 1580-1527* cm^{-1} and 1402-1366 cm^{-1} which are due to the carboxylato group. Additional bands at ~1300 cm^{-1} have been attributed to the metal-carboxylate linkage (O-C-O-M). These salicylato and nitrosalicylato derivatives do not show any i.r. bands in the region 1357-1310 cm^{-1} (showing absence of free phenolic group), but exhibit absorption bands at 1580 cm^{-1} and ~1380 cm^{-1} indicating that both phenolic as well as carboxylic group hydrogen atoms have been replaced. Absorption band at ~1300 cm^{-1} may be due to metal-carboxylate linkage while another band at ~ 1480 cm^{-1} may be assigned to the metal-phenoxy linkage. Further support for the structure of the salicylato derivatives can be derived from the comparison between the i.r. spectra of these derivatives and those of (i) monosalicylato molybdenum (VI)-oxo dichloride, $(C_7H_4O_3)MoOCl_2$ and (ii) disalicylato molybdenum (VI)-oxide $(C_7H_4O_3)_2MoO$ (these have been prepared by refluxing a *one* mole proportion of $MoOCl_4$ with one and two mole proportions respectively of salicylic acid in bezene, until the evolution of hydrogen chloride ceased). The compounds (i) and (*ii*) thus obtained show bands neither in the region ~3600 cm^{-1} nor in the region 1357-1310 (indicating absence of the free phenolic group), but show bands at 1565 cm^{-1} (1586-27 cm^{-1} region) and at 1380 cm^{-1} (1402-1360 cm^{-1} region) due to carboxylate group and at ~1280 cm^{-1} (in the region ~1300 cm^{-1}) due to a metal carboxylate linkage. Metal-phenoxy linkage band is observed at 1475 cm^{-1}.

A very sharp band at 980 cm^{-1} observed in these compounds is due to Mo=O stretching frequencies. The sharp bands at 1548-1520 cm^{-1} and 1360-1337 cm^{-1} are due to the presence of nitro groups.[15]

The following tentative structure may be proposed for the salicylato derivatives.



Acknowledgement

The authors are thankful to the Head of the Chemistry Department, University of Delhi, Delhi-110 007, for providing necessary facilities for work.

References

1. Arthur Rosenheim, Richard Schnabel and Robert Bilecki, *Ber.*, 1915, 48, 447.
2. Arthur Rosenheim and Richard Schnabel, *Ber.*, 1905, 38, 2777.
3. G. Illari, *Ann. Chim. Applicata.*, 1940, 30, 65.
4. K. L. Jaura and P. S. Bajwa, *J. Sci. Ind. Research*, 1961, 20B, 391.
5. Sarjoo Prasad and K. S. R. Krishnaiah, *J. Indian Chem. Soc.*, 1961, 38, 153.
6. Sarjoo Prasad and K. S. R. Krishnaiah, *J. Indian Chem. Soc.*, 1961, 38, 763-4.
7. S. N. Misra, *Indian J. Chemistry*, 1967, 5, 508.
8. G. A. Barbieri and R. Atti, *Accad. Lincei*, 1915, 24, 605-610; *J. Chem. Soc.*, (Abs.), 1915, A, i, 538.
9. S. P. Anand, R. K. Multani and B. D. Jain, *J. Organometal. Chem.*, 1970, 24, 428.
10. S. P. Anand, R. K. Multani and B. D. Jain, *Curr. Sci.*, 1968, 37, 487.
11. A. N. Meldrum and N. W. Hirve, *J. Indian Chem. Soc.*, 1928, 5, 95.
12. H. C. Barany and M. Pianka, *J. Chem. Soc.*, 1946, 965.
13. R. Mendola, H. S. Foster and R. Brightman, *J. Chem. Soc.*, 1917, 111, 539.
14. Satya Paul, Thesis, University of Delhi, Delhi, February, 1972.
15. S. K. Anand, Thesis, University of Delhi, Delhi, April, 1972.
16. M. Davies and R. L. Jones, *J. Chem. Soc.*, 1954, 120.
17. A. K. Babko and N. P. Evtushenko, *Ukr. Khim. Zh.*, 1969, 35(3), 295; (Russian); *C. A.*, 71, 8015 v.
18. John F. Brown Jr., *J. Amer. Chem. Soc.*, 1955, 77, 6341.

J. Indian Chem. Soc.,
Vol. LVII, February 1980, pp. 127-129

Transition Metal Complexes of Cinnamoylhydrazine

M. M. MOSTAFA, S. M. HASSAN and A. A. EL-ASMY

Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt

Manuscript received 5 March 1979, accepted 29 December 1979

Cinnamoylhydrazine (CH) form complexes with Co(II), Ni(II), Mn(II), Fe(III), Cr(III), Zn(II), Cd(II), and Hg(II). Their structures have been proposed on the basis of analytical, conductance and infrared data. Hg(II), Cd(II), Mn(II) and Zn(II) complexes coordinate via carbonyl oxygen and NH_2 groups, while Co(II), Ni(II), Fe(III) and Cr(III) complexes coordinate through the imidol structure. Spectral data confirm the tetrahedral structure for cobalt chloride and bromide, a square planar structure for Ni and an octahedral structure for Cr.

OUR earlier work[1-5] on the complexes of hydrazide has been extended to the complexes of cinnamoylhydrazine ($C_6H_5.CH{=}CH.CONHNH_2$) with some transition metal ions. In this paper we report the preparation and characterization of Co(II), Ni(II), Fe(III), Cr(III), Zn(II), Cd(II) and Hg(II) complexes of cinnamoylhydrazine.

Experimental

Materials and Methods :

All the chemicals were of AR or C.P grades. Cinnamoylhydrazine was prepared by the method described in the literature[6].

Preparation of the Complexes :

1:1, 1:2 and 1:3 M:L complexes were prepared by refluxing equimolar amounts of CH and the metal salts in ethanolic solution. The precipitation of the complexes was aided by digestion on a water bath for about one hour. The resulting precipitate was filtered, washed with hot ethanol and then dried in a desiccator over anhydrous calcium chloride.

Analysis :

The analyses for the metals and halides were carried out by the standard methods[7-8]. Hydrazine was estimated volumetrically by Jaimesons method[9]. Carbon and hydrogen analysis were performed by the Micro-analytical Unit at the University of Cairo. The analytical data are given in Table 1.

Physical Measurements :

IR spectra (4000-625 cm^{-1}) were recorded on a Pye Unicam SP. 2000 Spectrophotometer. Electronic spectra were recorded on a Pye Unicam SP. 1800 Spectrophotometer. Molar conductance measurements were carried out on Tacussel conductivity bridge type CD 6 NG with cell constant 0.97 cm^{-1} in DMF at concentration $10^{-3}M$.

Results and Discussion

The bonding sites in cinnamoylhydrazine complexes have been established by a comparison of their infrared spectra with that of the parent ligand.

Cinnamoylhydrazine reacts with Mn(II), Cd(II), Zn(II) and Hg(II) salts (I–XI) in the keto form as shown by the presistance of amide II band in the spectra of the complexes. The amide I band was shifted to a lower frequency by $\simeq$10-20 cm^{-1}. Similar behaviour has been reported earlier for metal (II)-semicarbazide[10], semicarbazone[10] and some substituted benzylidene aroylhydrazine[11]. Also, the NH_2 bending vibration band is shifted to a lower frequency by $\simeq$20-30 cm^{-1}. In these metal chelates the ligand being bidentate coordinate via NH_2 and C=O groups.

In the spectra of the complexes (XII to XVIII), amide I band at 1680 cm^{-1} in the spectrum of the ligand was displaced in the complexes. The amide II band at 1555 cm^{-1} disappeared and a strong band at 1530 cm^{-1} appeared. This may be attributed to ν(C=N)[12] formed as a result of enolization of the hydrogen of NH group to its adjacent carbonyl. In the spectra of these complexes a ν(-C-O-)[13] was observed at 1070 cm^{-1} together with an OH bending frequency at $\simeq$1200 cm^{-1} which indicate that the ligand has been reacted in the imidol structure.

Electronic Spectra :

The electronic spectra of Co(II), Ni(II) and Cr(III) complexes are reported in Table 2. The absorption spectra in DMF are similar to those in mujol mull indicating that their no difference in stereochemistry between the solid and the solution.

Visible spectra of the complexes XII, XIII and XIV show two bands in the range 16181-16234 and 14663 cm^{-1} indicating thus tetrahedral complexes for Co(II)[4,15]. Ni complexes (XV and XVI) show only one band in the region 22222-16667 cm^{-1} suggesting

TABLE 1—PHYSICOCHEMICAL DATA OF THE COMPLEXES

No.	Compound	M.P.	Colour	% Calculated C	H	Cl or Br	Metal	N_2H_4	% Found C	H	Cl or Br	Metal	N_2H_4	Molar conductance in DMF
	CH	101	Yellowish-white	66.64	6.21	—	—	19.76	66.41	6.13	—	—	19.70	—
I	$Hg(CH)Cl_2.H_2O$	>260	dirty white	23.93	2.68	15.70	44.41	7.09	23.30	2.40	15.57	44.66	6.54	13.5
II	$Zn(CH)Cl_2.2H_2O$	>260	white	32.31	4.22	21.19	19.68	9.60	31.90	4.00	21.13	20.20	10.08	16.5
III	$Zn(CH)_2Cl_2$	>260	,,	52.06	4.85	11.38	10.57	12 20	52.60	4.60	10.70	9.90	12.60	130.00
IV	$Zn(CH)Br_2.2H_2O$	>260	,,	25.49	3.33	37.71	15.42	7.50	24.40	3.70	37.03	15.63	6.61	18.5
V	$Zn(CH)_2.Br_2$	>260	yellow	39.34	3.67	29.09	11.88	11.60	39.10	3.30	30.12	9.63	10.19	26.10
VI	$Cd(CH)Cl_2.2H_2O$	>260	white	28.33	3.70	18.58	29.64	8.40	28.10	3.80	18.65	28.80	9.20	20.20
VII	$Cd(CH)_2Cl_2.2H_2O$	>260	,,	45.95	4.85	10.02	15.87	13.50	46.20	5.00	9.60	15.45	12.93	140.30
VIII	$Cd(CH)Br_2$	>260	pale yellow	24.88	2.32	36.79	25.87	7.30	24.40	2.00	36.07	25.93	8.80	18.90
IX	$Cd(CH)_2Br_2$	>260	,, ,,	36.24	3.38	26.80	18.84	10.70	36.30	23.00	26.01	19.23	9.39	22.40
X	$Mn(CH)Cl_2.2H_2O$	210	white	33.36	4.35	21.88	16.95	9.89	33.20	4.10	20.20	6.01	10.36	12.50
XI	$Mn(CH)_2Cl_2$	235	,,	48.02	4.48	15.75	12.02	12.45	47.90	4.60	15.30	13.01	13.30	13.50
XII	$Co(CH)Cl_2.H_2O$	>260	grey	34.86	3.90	22.87	19.01	10.33	33.70	3.40	22.20	19.60	10.40	21.60
XIII	$Co(CH)_2Cl_2.2H_2O$	>260	rose	44.10	4.93	14.46	12.02	13.02	44.20	4.50	14.26	11.90	13.38	28.90
XIV	$Co(CH)Br_2.2H_2O$	>260	,,	25.92	3.38	38.32	14.13	7.70	26.60	3.40	38.80	13.91	7.43	23.50
XV	$Ni(CH)_2Cl_2.H_2O$	>260	dull green	45.80	4.70	15.02	12.43	13.58	45.40	4.30	15.90	12.03	13.40	33.60
XVI	$Ni(CH)Cl_2$	>260	,, ,,	37.04	3.45	24.30	20.10	10.90	37.60	3.70	23.70	21.00	10.64	18.40
XVII	$Fe(CH)Cl_2.2H_2O$	>260	brown	29.99	3.91	29.51	15.49	8.89	30.20	4.10	29.99	14.69	8.63	20.55
XVIII	$Cr(CH)Cl_2.5H_2O$	>260	grey	25.21	4.70	24.81	—	7.05	26.50	4.70	24.72	—	7.32	19.60

TABLE 2—ELECTRONIC SPECTRAL DATA

Complexes	Soln.(a) cm^{-1}	nm	ε	Solid cm^{-1}	nm
1–$Co(CH)Cl_2.H_2O$	16181	618	370	16129	620
	14663	682	500	15152	660
2–$Co(CH)_2Cl_2.2H_2O$	16234	616	380	16252	615
	14663	682	515	15385	650
3–$Co(CH)Br_2.2H_2O$	–	–	–	16393	610
				15504	645
4–$Cr(CH)Cl_2.5H_2O$	–	–	–	17860	560
5–$Ni(CH)Cl_2$	–	–	–	16667	600
6–$Ni(CH)_2Cl_2.H_2O$	–	–	–	17241	580

(a) data obtained in DMF solution.

therefore a square planar configuration[16,17]. Cr complex (XVIII) show only one band around 17000 cm^{-1} which is in a good agreement with the values for octahederal Cr(III) complexes reported in the literature[18-20].

Conductance Measurements :

The molar conductance values (Λ_m) in DMF at the concentration 10^{-3} *M* are relatively low and are comparable to those of non-electrolytic solutions. However, two exceptional cases were recorded for Zn(II) and Cd(II) (structure III and VII), where values of 150 and 140.3 $ohm^{-1}cm^{-2}M^{-1}$ have been measured for Zn(II) and Cd(II) respectively high values indicate the occurance of two chlorine ions in DMF.

References

1. M. N. H. MOUSSA, F. I. M. TAHA and M. M. MOSTAFA, *Egypt J. Chem.*, 1973, **16**, 115.
2. F. I. M. TAHA, M. N. H. MOUSSA and M. M. MOSTAFA, *Egypt. J. Chem.*, 1973, **16**, 209.

3. I. M. ISSA, M. N. H. MOUSSA, F. I. M. TAHA and M. M. MOSTAFA, *7th Arab. Sci. Congr.*, 1973, 111, 131.

4. F. I. M. TAHA, M. N. H. MOUSSA, A. M. SHALLABY and M. M. MOSTAFA, *J. Acta. Chimica* (Budapest), 1976, 90, 73.

5. M. M. MOSTAFA, S. M. HASSAN and A. A. EL-ASMY, *J. Indian Chem. Soc.*, 1978, 55, 529.

6. P. P. SAH, *Rec. Trav. Chim.*, 1940, 59, 1036.

7. A. I. VOGEL, "Text Book of Quantitative Inorganic Analysis" (Longmans, Green & Co. Ltd., London), 1961, 380.

8. TREADWELL and HALL, "Analytical Chemistry" Vol. 11, John Wiley, New York, 1958.

9. G. S. JAMIESON, *Am. J. Sci.*, 1912, 33, 352.

10. L. EL-SAYED and M. F. ISKANDER, *J. Inorg. Nuclear Chem.*, 1971, 33, 345.

11. H. EL-KHADEM, M. F. ISKANDER and S. E. ZAYEN, *Z. Anorg. Allg. Chem.*, 1963, 320, 261.

12. L. D. FREDRICKSON, *Analyt. Chem.*, 1964, 36, 1349.

13. H. HAMADA, *Bull. Chem. Soc. Japan*, 1959, 32, 1051.

14. S. GURRIERI, A. SEMINARA, G. SRIAWSA and N. CUCINOTTA, *J. Inorg. Nuclear Chem.*, 1976, 38, 239.

15. F. A. COTTON and G. W. WILLKINSON, "Advanced Inorganic Chemistry", (John Wiley, New York), 1962.

16. P.V. BABYKUTTY, C.P. PRABHAKARAN, R. ANANTARAMAN and C. G. R. NAIR, *J. Inorg. Nuclear Chem.*, 1974, 36, 3685.

17. C. V. BANKS and D. W. BARNUM, *J. Amer. Chem. Soc.*, 1958, 80, 4767.

18. K. S. FRAPKELSTERIN and J. H. VAN VLECK, *J. Chem. Phys.*, 1940, 8, 790.

19. U. SARFORI, E. CERRONE and P. CAMCELLIER, *Acad. Linci. Res. Sci. Fix. Mat.*, 1963, 35, 226.

20. K. NAKAMOTO and P. J. McCARTHY, "Spectroscopy and Structure of Metal Chelate Compounds" (John Wiley, New York), 1968.

J. Indian Chem. Soc.,
Vol. LVII, February 1980, pp. 130-133

Metal Complexes of Fluorescein

BHARATI AGARWAL, BADRI VISHAL AGARWALA and ARUN K. DEY*

Chemical Laboratories, University of Allahabad, Allahabad-211 002

Manuscript received 24 July 1979, accepted 30 December 1979

Fluorescein forms complexes of type M Fl. xH_2O with Co(II), Zn(II), Cd(II) and Pb(II), while metal ligand ratios are 2:5, 2:5 and 3:4 for Ce(III), Th(IV) and UO_2(VI) complexes respectively. The complexes isolated from an aqueous medium are insoluble in common organic solvents suggesting their polymeric nature. This is supported by their high decomposition temperatures.

IR studies reveal that all the three possible donor sites i.e. carbonyl, phenolate and carboxylate groups are utilised in coordination, the oxygen-metal linkages being of different strengths. From uv-vis spectral and magnetic studies of Co(II) complex a distorted squarepyramidal symmetry seems probable. An interesting observation made is that the temperature of the commencement of loss of water molecules is inversly related to the νOH values of the complexes, leading to the conclusion that stronger the H-bonding, lesser is the tendency of the loss of water molecules.

IN an earlier publication[1] the results of investigation on the Cu(II) complex of fluorescein obtained in an aqueous medium have been reported. Fluorescein forms solid complexes with a number of other metal ions also, and here the Co(II), Zn(II), Cd(II), Pb(II), Ce(III), Th(IV) and UO_2(VI) complexes and their characteristics are being described.

Experimental

Materials : Aqueous solutions of $CoSO_4.7H_2O$ (BDH AnalaR), $ZnSO_4.7H_2O$ (E. Merck), $3CdSO_4.8H_2O$(Albright & Wilson), $Pb(NO_3)_2$ (BDH AnalaR), $Ce_2(SO_4)_3$ (BDH), $Th(SO_4)_2$ (BDH), $UO_2(NO_3)_2.6H_2O$ (Baker AR) and fluorescein disodium salt $Na_2C_{20}H_{10}O_5$ (M & B Indicator) were prepared. Dil. mineral acid (1 or 2 drops) was added to the metal solutions to prevent hydrolysis.

Isolation of the Complexes : Since the free dye (acid form) precipitates in an acidic medium, the solution of the metal ion was kept in excess while precipitating the metal derivative of fluorescein. Hence, to 100 ml of 0.04 *M* metal solution, 50 ml of 0.04 *M* fluorescein was added dropwise with constant stirring. The complexes precipitated instantaneously, they were allowed to settle, filtered, washed with water and dried at room temperature.

Empirical formula : Microdetermination of C & H was done as usual. The amount of metal was known from the weight of residue left on ignition, wherever possible.

Spectral studies : IR spectra were recorded on a Grating Infrared-Perkin Elmer Spectrophotometer Model 577 using KBr pellets in the range 4000-400 cm^{-1}.

Uv-vis electronic reflectance spectra (ers) were obtained on a mannual reading VSU-2P spectrophotometer using MgO as a reference.

Thermal studies : The tg results were obtained by heating at 10 min^{-1}.

Magnetic measurements : Magnetic measurements were done at room temperature (~30°) by Faraday method.

Results and Discussion

Composition and colour : Results on the composition and colour of the complexes are recorded below (Table 1).

TABLE 1—RESULTS OF ELEMENTAL ANALYSES AND COLOUR OF METAL FLUORESCEIN COMPLEXES

Empirical Formula	Colour	Carbon % Obs. (Calc.)	Hydrogen % Obs. (Calc.)
$CoC_{20}H_{10}O_5.3.5H_2O$	Dark brown	52.80 (53.08)	4.15 (3.76)
$ZnC_{20}H_{10}O_5.2.5H_2O$	Brick red	54.83 (54.42)	3.84 (3.40)
$CdC_{20}H_{10}O_5.3.5H_2O$	Light brick red	47.73 (47.43)	3.81 (3.36)
$PbC_{20}H_{10}O_5.H_2O$	Orange	43.60 (43.24)	2.32 (2.18)
$Na_4Ce_2(C_{20}H_{10}O_5)_5.13.5H_2O$	Red brown	53.15 (52.98)	3.96 (3.40)
$Na_2Th_2(C_{20}H_{10}O_5)_5.11H_2O$	Orange	51.31 (50.89)	3.10 (3.05)
$Na_2(UO_2)_3(C_{20}H_{10}O_5)_4.11H_2O$	Red	40.22 (40.14)	2.98 (2.67)

*For correspondence.

Ignition residues : On ignition of the complexes in air corresponding metal oxides are expected as residues. In the cases of Co(II), Zn(II) and Pb(II) complexes, the amount of the residues correspond to oxides. Since, Ce(III), Th(IV) and UO_2(VI) complexes contain Na also, the residues consist of a mixture of oxides (Table 2). In general, the metal contents calculated from the residues correspond with the empirical formulae. Discrepancy in the case of cadmium complex is probably due to possible sublimation of CdO at higher temperatures([2]).

TABLE 2—IGNITION RESIDUES

Complex	Material on ignition	Amount taken (mg)	Residue Obs. (Calc.)	Metal % Obs. (Calc.)
Co(II)-FL	Co_3O_4	4.040	0.740 (0.720)	13.45 (13.02)
Zn(II)-FL	ZnO	3.959	0.750 (0.731)	15.22 (14.83)
Cd(II)-FL	CdO	4.075	0.610 (1.035)	13.10 (22.22)
Pb(II)-FL	PbO	3.990	1.678 (1.603)	38.86 (37.30)
Ce(III)-FL	$2CeO_2+2Na_2O$	3.945	0.800 (0.815)	12.14 (12.39)
Th(IV)-FL	$2ThO_2+Na_2O$	3.855	0.940 (0.965)	19.17 (19.63)
UO_2(VI)-FL	$U_3O_8+Na_2O$	3.739	1.440 (1.422)	30.42 (29.85)

Solubility : The complexes do not dissolve in common organic solvents viz. ethanol, chloroform, ether, carbon tetrachloride, *n*-hexane, benzene and nitrobenzene etc. They are sparingly soluble in dimethylformamide and dimethylsulphoxide. The insolubility suggests their polymeric nature[3,4,5].

Infrared spectra : The important IR bands of the ligand are compared with those of the complexes (wave numbers are expressed in cm^{-1}) Table 3.

A band at 1678 in the ligand, assigned to νC=O, is not observed in the complexes in this region. This band generally shifts to lower frequencies on complexation[6,7,8], here it gets overlapped with ν_{asy} COO-band and therefore is not prominently located. In some cases it appears as a shoulder on this band. The shift in νC=O is taken as a measure of the strength of M–O bond[7,8,9] and greater the shift in νC=O, stronger is the M–O bond. Thus the complexes of different metal ions may be arranged in order of strength of M–O bond (related to C=O bond) as :

$$Co(II) < Pb(II) < Ce(III) < UO_2(VI)$$

The νC–O$^-$ (phenolate) band observed in the ligand at 1310 shows a shift to higher frequencies in all the complexes, indicating its involvement in complexation[10]. Also greater the shift, stronger is the M–O bond[11]. Thus the complexes may be arranged in order of strength of M–O (phenolate) bond as follows :

$$Co(II) < Th(IV) < Cd(II) < Pb(II) < Ce(III) \sim UO_2(VI) < Zn(II)$$

In all the complexes $\nu_{asy}COO^-$ (at 1593) decreases while a very slight increase is observed in ν_{sy} COO^- (at 1382). Hence COO^- to metal link is predominantly ionic in nature. The relative values of $\nu_{asy}COO^-$ give an indication of the proportion of ionic character of the link[12,13]. Thus the order of increasing ionic character is—

$$Zn(II) \sim Co(II) < Ce(III) < UO_2(VI) < Pb(II) \sim Cd(II) \sim Th(IV)$$

Two strong bands in the ligand at 1260 and 1240 may be assigned to ν(C–O–C)[14]. They are not separately observed in the complexes and show positive shift on complexation, excluding the possibility of the coordination of this oxygen to metal in such cases[15,16].

TABLE 3—IMPORTANT IR BANDS OF FLUORESCEIN AND ITS COMPLEXES*

	$\nu OH(H_2O)$	νC=O	δH_2O/ring	$\nu_{asy}COO^-$	$\nu_{sy}COO^-$	νC-O$^-$	ν(C-O-C)
Na_2FL	3280-3200b, w	1690-75b	1635m	1592vs	1385s	1310s	1260, 1240s
Co(II)-FL	3480b, m	1552 s	1635sh	1578s	1388s	1312sh	1275s
Zn(II)-FL	3420b, m	—	1630m	1578s	1390s	1328s	1275sh
Cd(II)-FL	3570b, m	—	1630m	1570s	1388s	1322s	1281s
Pb(II)-FL	3440b, m	1545sh	1630m	1570s	1388s	1324s	1282s
Ce(III)-FL	3420b, m	1540sh	1633m	1577s	1390s	1325s	1303s
Th(IV)-FL	3420b, m	—	1630m	1570s	1385s	1320s	1295s
UO_2(VI)-FL	3460b, m	1533m	1630m	1575s	1390s	1325sh	1282s

*s-strong, m-medium, w-weak, sh-shoulder, b-broad.

Since the ligand is hygroscopic, bands due to $\nu OH(H_2O)$ and δH_2O or/and ring vibrations[17] appear at 3280-3200 and 1635. Occurrence of these bands in all the complexes indicates the presence of lattice and/or crystallisation and/or coordination water[17]. Very broad nature of OH bands probably suggests different types of H-bonding which may be a consequence of several oxygens in the ligand. However, no bands could be observed in the region 1100-700 assignable to wagging, twisting and rocking modes of H_2O, showing that the nature of metal to oxygen (of H_2O) link is not predominantly covalent.

A strong band at 918 observed only in UO_2(VI) complex is the well known ν_3 band of UO_2 (VI) ion, a characteristic feature of all uranyl complexes[14].

The structure of the fluorescein shows the three coordinating sites being so distantly situated that the possibility of any two sites being linked to same metal may completely be ruled out. Therefore, each site will most probably be linked to an independent metal atom and other coordination numbers of the metal will then be satisfied with different ligand molecules, thus producing a continuous three dimensional polymeric structure.

Electronic refllectance spectra: The ers of the ligand has a strong band (I) with its λ_{max} at 530 nm with three minor peaks on the lower wavelength side at 500 nm (Ia), 350 nm (Ib) and 270 nm (Ic), while the absorbance becomes zero at 235 nm. On the higher wavelength side absorbance decreases more rapidly but it does not vanish up to 900 nm.

In the ers of the complexes excepting Co(II), only intraligand bands are expected and any changes in the ers of these complexes may be ascribed to the ligand itself, while in the case of Co(II) complex bands due to metal ion in the ligand field are also expected. The ers of all the complexes show that in general band I moves to lower wavelengths (500-525 nm). While Ia could not be observed in any of the complexes, bands Ib and Ic generally move to lower values. However Pb(II) complex is peculiar in exhibiting a strong band at 360 nm.

Before discussing ers and symmetry around the metal ion it must be emphasized that although all donor atoms are oxygens, they are non-equivalent to each other and therefore, a perfect symmetry is completely ruled out[18].

The ers of Co(II) when compared to that of other complexes, reveal three additional bands – first at ~390 nm, second at ~590 nm with a shoulder on its higher wavelength side and a third band of much weaker intensity of 875 nm. When these spectral bands of Co(II) are compared with the literature data[19,20], it is concluded that these neither compare with octahedral complexes, nor with tetrahedral complexes or with square planar complexes. However, according to Lions et al.[21] a weak band at 875 nm is characteristic of square pyramidal complexes. In similarity to the reported spectrum for Co(II) squarepyramidal complex by Ciampolini et al.[22], the observed bands may be assigned as—

Bands	*Assignment*
390 nm (25.64 kK)	$^4A_2 \rightarrow {}^4B_1$
590 nm (16.95 kK)	$\rightarrow {}^4B$
875 nm (11.43 kK)	$\rightarrow {}^4A_2$

Ciampolini and Nardi[23] in another communication found that suitable ligands for high spin five coordination should fulfill two main conditions: (a) donor atoms must possess strong coordinating ability and little tendency to form π-bonds and (b) the ligand must be bulky and polydentate one so that crowding around the metal ion should prevent a six coordinated configuration being attained. It may be seen that, fluorescein, satisfies both these conditions.

According to Gillespie[24], among the penta-coordinated transition metal ions, trigonal bipyramid symmetry is favoured in largely covalent complexes, while essentially ionic bonding favours squarepyramid symmetry and an intermediate structure is expected when bonding is intermediate in character. In the present complexes, as the ir study indicates, the bonding character (on the whole) is expected to be on the ionic side which further lends support to the distorted squarepyramid symmetry.

Magnetic study: The effective magnetic moment for Co(II) complex has been determined to be 4.77BM. But the value is at the lower limit of the range 4.7 - 5.2 BM observed for octahedral complexes and at the upper limit of the range 4.4 – 4.8 BM observed for tetrahedral complexes[25]. For squareplanar complexes range is generally 4.8 – 5.2 BM. However, the observed moment is similar to some other Co(II) complexes having distorted squarepyramidal geometry[21].

Thermogravimetric study: All the complexes contain water molecules, and generally in the primary stage of heating, these water molecules are expected to be lost. Excepting the case of cerium complex, in all others it is observed that in the initial stage slow

TABLE 4—THERMAL DATA OF FLUORESCEIN COMPLEXES

Complex	T_i(°)	T_d(°)
Co(II)-FL	40	280
Zn(II)-FL	80	380
Cd(II)-FL	40	320
Pb(II)-FL	120	340
Ce(III)-FL	60	–
Th(IV)-FL	60	360
UO_2(VI)-FL	60	340

weight loss occurs, which corresponds to water present in the respective complex. After this fast decomposition sets in. Table 4 records the starting temperature of initial stage weight loss (T_i) and decomposition temperature (T_d) for the complexes. In case of cerium complex this type of two distinct stages could not be observed.

From the Table 4, it may be seen that water loss starting at lower temperatures continues upto quite high temperatures. It appears that weight loss at lower temperature ranges is due to uncoordinated water molecules, whereas that at higher temperatures evidently signifies the loss of coordinated water. However, from the tg curves the two types could not be distinguished.

From Table 4, following is the order on the basis of T_i :

$$Cd(II) \sim Co(II) < UO_2(VI) \sim Ce(III) \sim Th(IV) < Zn(II) < Pb(II)$$

From the IR data (Table 3), the order on the basis of νOH in the different complexes is :

$$Cd(II) > Co(II) > UO_2(VI) > Pb(II) > Ce(III) \sim Th(IV) \sim Zn(II)$$

The above two orders are reverse to each other (Pb (II)-exception). Since lower νOH values indicate stronger H-bonding, it appears that the complexes having stronger H-bonding lose water molecules at higher temperatures.

Decomposition temperatures, T_d, for all the complexes are quite high (Table 4), which further support the polymeric nature. The decompositions of cerium, thorium and uranyl complexes are not complete even at 800° whereas for most of the reported complexes of these metal ions, the oxide level is reached at much lower temperatures[2].

Acknowledgement

The authors are thankful for the support received from the University Grants Commission, New Delhi.

References

1. B. Agarwala, B. V. Agarwal and A. K. Dey, *J. Indian Chem. Soc.*, 1979, **56**, 342.
2. C. Duval, Inorganic Thermogravimetric Analysis, Elsevier, Amsterdam, 1963.
3. B. P. Block, in "Inorganic Polymers", (Eds.) F. G. A. Stone and W. A. G. Graham, Academic Press, New York, 1962.
4. W. C. Fernelius. WADC (Wright Air Develop. Centre) Tech. Rept. 1956, 56/203.
5. V. Banerjie and A. K. Dey, *Makromol. Chem.*, 1979, **180**, 2133 ; P. L. Maurya, B. V. Agarwala and A. K. Dey, *Indian J. Chem.*, 1978, **16A**, 258.
6. E. M. Briggs and A. E. Hill, *J. Chem. Soc.*, A, 1969, 1835.
7. G. C. Percy and D. A. Thornton, *J. Inorg. Nuclear Chem.*, 1973, **35**, 2719.
8. R. West and R. Riley, *J. Inorg. Nuclear Chem*, 1957, **5**, 295.
9. H. F. Holtzclaw, Jr. and J. P. Collman, *J. Amer. Chem. Soc.*, 1957, **79**, 3318.
10. R.N. Prasad and J.P. Tandon, *J. Inorg. Nuclear Chem.*, 1974, **36**, 1473.
11. T. R. Harkins, J. L. Walter, O. E. Harris and H. Freiser, *J. Amer. Chem. Soc.*, 1956, **78**, 263.
12. A. J. Saraceno, I. Nakagawa, S. Mizushima, C. Curran and J. V. Quagliano *J. Amer. Chem. Soc.* 1958, **80**, 5018.
13. M. J. Schmelz, I. Nakagawa, S. Mizushima and J. V. Quagliano, *J. Amer. Chem. Soc.*, 1959, **81**, 287.
14. C. N. R. Rao, Chemical Applications of Infrared Spectroscopy, Academic Press, New York, 1963.
15. I. S. Ahuja and A. Garg, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 937.
16. G. C. Pellacani, R. Battistuzzi and G. Marcotrigiano, *J. Inorg. Nuclear Chem.*, 1973, **35**, 2243.
17. K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, John Wiley, New York, 1963.
18. T. M. Dunn, in "Modern Coordination Chemistry" (Eds) J. Lewis and R. G. Wilkins, Interscience, New York, 1960.
19. F. A. Cotton and R. H. Holm, *J. Amer. Chem. Soc.*, 1960, **82**, 2979.
20. A. B. P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, 1968.
21. F. Lions, I. G. Dance and J. Lewis, *J. Chem. Soc.*, A, 1967, 565.
22. M. Ciampolini and I. Bertini, *J. Chem. Soc.*, A, 1968, 2241.
23. M. Ciampolini and N. Nardi, *Inorg. Chem.*, 1966, **5**, 41.
24. R. J. Gillespie, *J. Chem. Soc.*, 1963, 4679.
25. M. C. Day and J. Selbin, Theoretical Inorganic Chemistry, Affiliated East West, New Delhi, 1971.

J. Indian Chem. Soc.,
Vol. LVII, February 1980, pp. 134-136

Be(II), Mg(II) and Ca(II) Complexes of Penicillins

(Km.) ANURADHA TIWARI, H. N. SHARMA

Chemical Laboratories, M.V.M., Ujjain

and

P. B. CHAKRAWARTI*

Chemical Laboratories, M.L.B. College, Bhopal

Manuscript received 16 April 1979, accepted 28 December 1979

The chelating behaviour of penicillins has been studied with the metal ions, Be(II), Mg(II) and Ca(II) using Bjerrum-Calvin pH titration technique, at three temperatures 20°, 30° and 40° in 50% (V/V) acetone-water mixture and an ionic strength of 0.1 M with $NaClO_4$. The proton ligand and metal ligand formation constants have been calculated by various computational methods. The order of stability obtained :Be(II) > Mg(II) > Ca(II) follows order of e^2/r, II nd ionisation potential, sum of Ist and IInd ionisation potentials and electro-negativities of the metals.

METAL complexes play an important part in the biological activity of a drug, since chelation with metal ions has been suggested one of the important mechanism for drug action[1,2]. Although chelating behaviour of many therauptic drugs has been reported in the literature, no information is available on chelation of metal ions with the two most common and widely used penicillins, penicillin-G (PG) and penicillin-V (PV). In the present investigation, stepwise proton-ligand stability constants and metal-ligand stability constants of the two penicillins with a carcinogenic metal ion Be(II) and two biologically active metal ions, Mg(II) and Ca(II) have been calculated by various computational methods described by Irving-Rossotti[3] using the Bjerrum-Calvin[4] pH titration technique as adopted by Irving and Rossotti[5]. Preliminary stoichiometric studies in solution were done using conductometric and potentiometric (pH) titrations employing the monovariation method[6].

Experimental

All the chemicals employed were of high purity. The solutions were prepared in doubly distilled water and standardised by appropriate standard methods.

Conductometric studies were done on WTW, LBR, Germany conductivity bridge, while pH measurements were done on 'Systronics' pH meter, No 322, using glass calomel electrode assembly in conjuction with saturated calomel electrode.

Penicillin-G or -V solution was prepared in 80% acetone-water (v/v) mixture, by percolating a solution of sodium/potassium salt of the same through a column of Amberlite, IR-120, cation exchanger resin (H^+-form) and washing the column with 80% acetone-water solvent. Penicillin (-G or -V) solutions thus obtained were then standardised with a standard alkali before use.

For potentiometric titrations, following mixtures, keeping the total volume 50 ml with 1 : 1 (V/V) acetone-water as solvent, were titrated against carbonate free 0.2 *M* KOH:

(A) 5 ml 0.04 *M* $HClO_4$

(B) Mixture (A) + 10 ml 0.02 *M* ligand solution

(C) Mixture (B) + 5 ml 0.002 *M* metal solution

The ionic strength was kept 0.1 *M* in each case by adding appropriate quantities of 1.0 *M* $NaClO_4$. Titrations were carried out in a specially designed 100ml cell, which has an outer jacket for circulation of water at a fixed temperature from a thermostat with a water circulating device. The cell had a plastic lid with appropriate holes to accomodate the electrodes burette nozzle and nitrogen bubbling device.

pH-meter readings obtained at a given alkali addition in duplicate titrations were reproducible with the maximum variation of 0.025 pH unit. Correction of pH in 50% acetone-water system was done as described by Van-Uitert and Hass[7] and Irving and Rossotti[5]. From the shifts in the pH titration curves values of $\bar{n}_A$, $\bar{n}$ and pL were calculated by Irving-Rossotti equations[3]. From $\bar{n}_A$ values of the ligands at various pH values, proton-ligand stability constant, K^H, for PG and PV were obtained by (a) the half integral method (From the plot of $\bar{n}_A$ vs pH), (b) point wise calculation, using the equation :

$$\log K_1^H = pH + \log \frac{\bar{n}_A}{1-\bar{n}_A}$$

and (c) the linear plot method (plotting $\log \bar{n}_A/1-\bar{n}_A$ vs pH). The result obtained are recorded in Table 1 and are found in aggrement.

*To whom correspondence should be made.

TABLE 1—PROTON LIGAND FORMATION CONSTANTS

(a) Half integral method (b) Linear plot method
(c) Point wise calculation method.

Ligand	log K_1^H 20°C	log K_1^H 30°C	log K_1^H 40°C	Method
PV	4.28	4.03	3.55	a
	4.28	4.03	3.50	b
	3.97	3.88	3.41	c
	(4.17)	(3.98)	(3.49)	
PG	5.00	4.93	4.45	a
	5.05	4.90	4.40	b
	4.82	4.50	4.28	c
	(4.88)	(4.77)	(4.37)	

The stepwise formation constants of the metal complexes were obtained by plotting formation curves, between the values of $\bar{n}$ and pL. The values of log K_1 and log K_2 were directly read from their formation curves. The refined values were obtained by the best least square fit. The result obtained are given in Table 2.

Results and Discussion

The values of proton-ligand formations constants, K_1^H, vary as : PG>PV (Table-1). This may be attributed to the difference in the electronegativity of the substituents in the side chains of the ligands. Presence of phenoxy-methyl group in PV, exerts greater electron with drawing effect than that of benzyl group in PG.

Preliminary conductometric and potentiometric(pH) titrations, using Nair and Pande's monovariation method[6] indicate formation of ML and ML_2 complexes with penicillins and the metals used in this investigation. The maximum values of $\bar{n}_A$ (≈ 2) also confirm the formation of two complexes, ML and ML[2].

Further, pH-titrations reveal that in all cases, only one proton is released during complexation of each molecule of any of the ligands. Thus the reactions may be represented as follows :

$$M^{++} + HL \rightleftharpoons ML^+ + H^+$$

$$ML^+ + HL \rightleftharpoons ML_2 + H^+$$

Where, M^{++} = Be(II), Mg(II) or Ca(II) and
HL = PG or PV.

TABLE 2—STABILITY CONSTANTS

$\mu = 0.1$ M ($NaClO_4$). (a) Half $\bar{n}$ method
(b) Least Square method

Ligand	Temp.	Method	Be(II) log K_1	Be(II) log K_2	Be(II) log β_2	Mg(II) log K_1	Mg(II) log K_2	Mg(II) log β_2	Ca(II) log K_1	Ca(II) log K_2	Ca(II) log β_2
PV	20°C	a	4.96	4.50	9.46	4.35	3.80	8.15	4.20	3.72	7.92
		b	(4.98)	(4.50)	(9.48)	(4.36)	(3.84)	(8.20)	(4.21)	(3.72)	(7.93)
	30°C	a	4.70	4.15	8.85	4.21	3.70	7.91	4.10	3.62	7.72
		b	(4.68)	(4.21)	(8.90)	(4.12)	(3.61)	(7.73)	(4.08)	(3.57)	(7.65)
	40°C	a	4.30	3.90	8.20	3.70	3.45	7.17	3.61	3.29	6.90
		b	(4.41)	(3.87)	(8.28)	(3.80)	(3.43)	(7.29)	(3.73)	(3.29)	(7.02)
PG	20°C	a	5.20	4.60	9.80	4.67	4.15	8.82	4.50	4.10	8.60
		b	(5.21)	(4.67)	(9.78)	(4.69)	(4.25)	(8.94)	(4.47)	(4.10)	(8.57)
	30°C	a	5.00	4.40	9.40	4.55	3.95	8.50	4.40	3.80	8.20
		b	(4.98)	(4.62)	(9.44)	(4.40)	(4.05)	(8.38)	(4.12)	(3.92)	(8.04)
	40°C	a	4.75	4.20	8.25	4.40	3.72	8.10	4.27	3.62	7.89
		b	(4.77)	(4.20)	(8.98)	(4.10)	(3.76)	(7.86)	(4,05)	(3.73)	(7.78)

With Be(II) and Mg(II) a precipitate was obtained on progressive addition of alkali during the titration. With PG at *p*H 5.7 and 4.5, while with PV at *p*H 5.6 and 5.5 respectively. This might be because of salt formation as experienced by Albert[8] in other systems. In these cases all the calculations have been done below the *p*H of precipitations. Further, with the use of very dilute solutions ($1\times10^{-4}M$) of the metals, possibility of the formation of polynuclear complexes may be ruled out.

A perusal of Table 2 clearly indicates that the order of the stability constants of the metal complexes (with the two ligands) follows the order of basic strength of the ligands used in this investigation i.e. PG complexes are more stable than the PV complexes. While, the order obtained with the metals and any of the ligands follows the order of atomic number, e^2/r-ratio, electronegativities, second ionisation potentials and the sum of the first and second ionisation potentials of the metals :

$$Be(II) > Mg(II) > Ca(II)$$

Acknowledgement

Authors' thanks are due to 'Glaxo Laboratories' and 'S. M. Chemicals, Baroda' for kindly supplying the free samples of penicillin-G.

References

1. MIKELAND ANDREWS, *J. Amer. Chem. Soc.*, 1955, 77, 5291.
2. C. D. CORYELL, 'Specal Problems in The Formation of metal complexes in chemical specificity in biological interaction' Ed. by R.N. Gurd., Academic Press, N. Y. 1954, p. 90.
3. H. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.*, 1953, 3397.
4. A. E. MARTELL and M. CALVIN, 'Chemistry of Metal Chelate Compounds', Prentice Hall, N. Y. 1953, p. 192.
5. H. M. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.*, 1954, 2904.
6. M. R. NAIR and C. S. PANDE, *Proc. Ind. Acad. Sci.*, 1948, 27A, 284.
7. A. ALBERT, *Biochem. J.*, 1953, 54, 246.

J. Indian Chem. Soc.,
Vol. LVII, February 1980, pp. 137-138

Co(II), Ni(II), Cu(II) and Zn(II) Complexes with Phenyl Urea

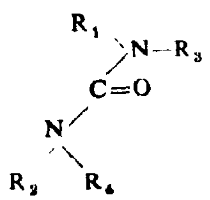
P. K. PANDA and B. K. MOHAPATRA

Department of Chemistry, Ravenshaw College, Cuttack-753 003

Manuscript received 9 August 1979, accepted 30 December 1979

A number of complexes having the general formula ML_2X_2 is described in which M^{+2}=Co, Ni, Cu and Zn, "L" stands for phenyl urea and $X=Cl^-$, Br^- or NO_3^-. These are characterised on the basis of analysis, conductance, magnetic susceptibility, infrared and electronic spectral data.

AMONG the ligands having a C=O group as the donor site, the amides and lactams are particularly interesting since these molecules possess also an amine group, which potentially may (also) act as a donor to the metal ion. However, with transition metal ions thus far only compounds have been isolated that contain oxygen co-ordinated lactams and amides. Earlier we have studied[1-3] the complexes of some lactams, dicyanadiamide and acrylamide. Introducing a second amine group in the ligand at the other side of the C=O group produces another type of ligands. This



class of ligands is also very interesting, since now three possible bonding sites are present which may yield several type of complexes e.g. monodentate via either oxygen or nitrogen, bridging bidentate via oxygen and nitrogen or bridging bidentate via two nitrogen atoms. In addition, hydrogen bonds with the anions may occur even when co-ordination via one nitrogen occurs. It was therefore thought worthwhile to study the complexation behaviour of phenyl urea with Co(II), Ni(II), Cu(II) and Zn(II) ions.

Experimental

All the chemicals used are of AnalaR grade. Ethanolic solution of metal salts was treated with ethanolic solution of phenyl urea in (1:2) molar proportion and it was refluxed for one hour. Resulting clear solution was kept overnight, when crystalline compounds were separated out. These were filtered under suction, washed with ethanol followed by ether

TABLE 1—ANALYTICAL DATA OF COMPLEXES

Compounds	M.P. (°C)	Λ_M (mhos. cm²)	μ_{eff} (B.M.)	% of metal Found	% of metal Calcd.	% of nitrogen Found	% of nitrogen Calcd.
1. CoL_2Cl_2	148	5.6	5.0	14.24	14.66	6.42	6.96
2. CoL_2Br_2	140	5.8	5.2	11.86	12.03	5.34	5.71
3. $CoL_2(NO_3)_2$	145	6.4	5.2	12.45	12.95	11.98	12.31
4. NiL_2Cl_2	202	5.5	3.0	14.26	14.61	6.51	6.97
5. NiL_2Br_2	195	7.8	3.0	11.58	11.99	5.32	5.71
6. $NiL_2(NO_3)_2$	140	8.2	3.3	12.56	12.91	11.82	12.31
7. CuL_2Cl_2	105	6.4	1.8	15.28	15.62	6.35	6.88
8. CuL_2Br_2	155	6.8	1.84	12.47	12.85	5.12	5.66
9. $CuL_2(NO_3)_2$	165	7.5	1.82	13.51	13.82	11.86	12.18
10. ZnL_2Cl_2	185	8.2	—	15.82	16.00	6.35	6.85
11. ZnL_2Br_2	178	8.4	—	12.82	13.17	5.26	5.64
12. $ZnL_2(NO_3)_2$	186	7.8	—	13.85	14.17	11.86	12.13

L=Phenyl Urea.

TABLE 2—INFRARED AND ELECTRONIC SPECTRA cm^{-1}

Compound No.	$\nu(C=O)$	$\nu(N-H)$	$\nu(M-O)$	$\nu(M-N)$	ν_{max} in k.k.(ϵ)
Ligand	1670	3400	—	—	—
1	1660	3380, 3290	455	260	19.0(45), 8.4(15)
2	1660	3390, 3290	450	260	19.2(45), 8.5(15)
3	1660	3380, 3300	445	265	19.0(40), 8.4(15)
4	1655	3390, 3280	450	255	9.0(5), 14.7(6), 24.5(16)
5	1650	3380, 3290	450	265	9.0(5), 14.9(6), 24.8(16)
6	1650	3390, 3300	455	270	9.0(5), 15.1(6), 24.8(16)
7	1665	3390, 3280	445	275	13.8(35)
8	1660	3375. 3270	450	265	14.0(38)
9	1660	3380, 3280	455	260	14.3(40)
10	1655	3390, 3280	425	280	—
11	1655	3390, 3300	430	275	—
12	1660	3380, 3290	430	280	—

and dried in vacuum desiccator. Metal in the complexes was estimated by E.D.T.A titration methods, nitrogen by micro analysis and conductance was measured in $M/1000$ acetone solution of the complexes using Toshniwal conductivity bridge. Magnetic susceptibility were measured by Gouy method. Infrared spectra were recorded in KBr phase using Beckman I.R.-20 and I.R.-12 spectrophotometer. Electronic spectra were recorded in M/100 (chloroform-ligand) solutions using Hilger watt uvispeck spectrophotometer. Relevant data are presented in Table 1 and Table 2.

Results and Discussion

All the complexes have the general formula ML_2X_2 where M^{+2} = Co, Ni, Cu and Zn, L=Phenyl urea and X is anion=Cl^- or Br^- or NO_3^-. These have relatively low melting points and are fairly soluble in acetone in which the molar conductance values are low indicating non-electrolytic nature. Magnetic moment of the complexes are in the range of 5.0 – 5.2, 3.0 – 3.3 and 1.8 – 1.84 B.M. for cobalt(II), nickel(II) and copper(II) complexes respectively indicating a spin free octahedral or distorted octahedral configuration.

All the cobalt(II) complexes are pink crystalline solids nickel(II) compounds are light green and copper(II) complexes are green solids.

Infrared spectra in the amide region have been frequently used for distinguishing between -O and -N co-ordination. $\nu(C=O)$ (amide-I band) usually occurs[4] in the 1650—1690 cm^{-1} region. In the ligand this has been observed at 1670 cm^{-1} and in the complexes this band was found ~1660 cm^{-1} indicating[5] co-ordination through the oxygen atom. Amide-II band is observed at 1620 cm^{-1} in the ligand and ~1600 cm^{-1} in the complexes. Further in the ligand ν(N-H) occured at 3400 cm^{-1} which splits and observed at a lower frequency region in the complexes ~3380 and 3290 cm^{-1}. Lowering may partly be due to hydrogen bonding with the anion. But from the consideration of the position and nature of ν(N-H) and amide-II band, bonding through the nitrogen of the-NH group is also expected. This has been further supported[6] by the observation of ν(M-O) and ν(M-N) 420-450 and 250-280 cm^{-1} regions in the far infrared spectra in agreement with earlier observation[7]. In case of nitrato complexes $\Delta\nu$(difference between ν_4 and ν_1 bands on co-ordination due to splitting of the ν_3 mode of ionic nitrate group) is of the order of ~130 cm^{-1} indicating[8] monodentate nitrate co-ordination.

The electronic spectra of cobalt(II) complexes in solution show two absorption bands ~19.0 (45) and 8.4 (15) k.k. regions attributable[9] to ${}^4T_{1g}$ (F)→${}^4T_{1g}$ (P) and ${}^4T_{1g}$→${}^4T_{2g}$ (F) transitions respectively. A spin free octahedral configuration is suggested for these complexes in conformity with magnetic moment data. Nickel(II) complexes give rise to three weak absorption bands ~9.0 (5), 14.7 – 15.1 (6) and 24.5 – 24.8 (16) k.k. regions assignable[10] to ${}^3A_{2g}$→${}^3T_{2g}$, →${}^3T_{1g}$, (F)→${}^3T_{1g}$ (P) transitions respectively and a spin free octahedral stereochemistry is presumed for these compounds basing on μ_{eff} values. In case of copper(II) complexes one broad absorption band is observed ~13.8 – 14.3 k.k. region suggesting a distorted octahedral configuration. Basing on analytical and spectral data zinc(II) complexes have also an octahedral environment around the metal ion.

Acknowledgement

Thanks are due to University Grants Commission, New Delhi for financial assistance.

References

1. P. K. PANDA and B. K. MOHAPATRA, *J. Inorg. Nuclear Chem. (London)*, In press.
2. C. D. RAO and B. K. MOHAPATRA, *J. Inorg. Nuclear Chem.*, 1977, 39, 689.
3. P. K. PANDA and B. K. MOHAPATRA, *Indian J. Chem* (communicated).
4. R. M. SILVERSTEIN and G. C. BASSLER, "Spectrometric identification of organic compounds", Wiley, New York, 1971.
5. J. REEDIJK, *Inorg. Chim. Acta*, 1971, 5, 687.
6. J. R. FERRARO, "Low frequency vibration of inorganic and co-ordination compounds", Plenum Press, New York, 1971.
7. J. REEDIJK, *Inorg. Chim. Acta*, 1975, 13, 219.
8. R. V. BIAGETTI, W. C. BOTTJER and H. M. HAENDLER, *Inorg. Chem.*, 1966, 5, 379.
9. B. N. FIGGIS, "Introduction to ligand fields", Wiley Eastern, New Delhi, 1976.
10. A. B. P. LEVER, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam, 1968.

J. Indian Chem. Soc.,
Vol. LVII, February 1980, pp. 139-141

N-α-Pyridyl-N′-Benzoyl Thiourea as a Chelating Agent for the Determination of Iridium

S. C. SHOME, M. MAZUMDAR and P. K. HALDAR

Presidency College, Calcutta-700 073, India

Manuscript received 20 July 1979, accepted 30 December 1979

N-α-pyridyl-N′-benzoyl thiourea (PBT) is recommended as the most suitable reagent for either gravimetric or spectrophotometric determination of iridium. The precipitate formed by the reagent with iridium(III) at *p*H 4.2-5.86 can be weighed as $Ir(C_{13}H_{10}N_3OS)_3$. The base metals do not interfere with the gravimetric determination of iridium in presence of masking agents. Interferences of platinum (IV) and palladium(II) are avoided by prior precipitation of the metal ions with PBT in 1.5(*N*) hydrochloric acid medium. Ruthenium(III) and osmium(VI) when reduced with hydroxylamine hydrochloride and sulphur dioxide respectively, produce no interference in the gravimetric determination of iridium. The iridium-PBT complex can be extracted with chloroform at *p*H 5.2-6.4 for the spectrophotometric determination of iridium. The extract shows maximum absorbance at 350 nm, obeys Beer's law at the same wavelength over the concentration range of the metal from 0.816 μg/ml to 8.16 μg/ml. By the use of PBT, iridium can be spectrophometrically determined in the presence of large amounts of all the base metals and noble metals except rhodium.

FEW organic reagents have been used for either gravimetry or spectrophotometry of iridium. Benzyltriphenyl phosphonium chloride[1], tetraphenyl arsonium chloride[1], 2-mercaptobenzothiazole[2], 2-mercaptobenzimidazole[3] were employed for the precipitation of iridium, but none of the reagents is suitable for direct gravimetry of the metal. Although *p*-nitrodimethyl aniline[4], dianisidine[5], tetraphenyl phosphonium bromide[6] and oximidobenzotetronic acid[7] were recommended for the spectrophotometry of the metal, their colour reactions are, however, easily affected by slight change in experimental conditions and the methods suffer from serious interferences caused by the presence of common acid radicals and other platinum metals. Iridium was determined by both gravimetry and spectrophotometry using thiosalicylamide[8] as the chelating agent. Some other platinum metals, however interfere.

In the present investigation N-α-pyridyl-N′-benzoyl thiourea[9-12] (PBT) has been found effective for the gravimetric as well as spectrophotometric determination of iridium. Iridium (III) is quantitatively precipitated with the reagent in the *p*H range 4.2–5.86 as an orange yellow complex which is stable towards heat, light, air and can be weighed directly as $Ir(C_{13}H_{10}N_3OS)_3$ for gravimetric determination of the metal. For the spectrophotometric determination of iridium the metal complex is extracted with chloroform at *p*H 5.2-6.4. Iridium can be determined with the reagent by both gravimetry and spectrophotometry in the presence of a large excess of base metals and noble metals except rhodium.

Experimental

Apparatus, Reagents and Chemicals :

A Carl Zeiss spectrophotometer, Model PMQ II, with 1-cm quartz cells, was used for transmittance measurements. A Cambridge Bench Model *p*H meter equipped with glass and calomel electrodes was used for *p*H measurements.

A standard iridium(III) solution was prepared by dissolving iridium trichloride, monohydrate (E. Merck) in dilute hydrochloric acid and standardizing the solution by hydrolytic precipitation method. Solutions of diverse ions were prepared by dissolving known amounts of the corresponding pure salts in distilled water or dilute hydrochloric acid.

All the reagents and chemicals used were of A. R. grade.

Properties and composition of the complex :

The iridium-PBT complex is stable towards heat, light, air and slowly decomposes at 172°. The complex was analysed for iridium, nitrogen and sulphur, and the analytical results were as follows :

Percentage found : Ir – 20.09, N = 13.19, S = 9.96.

Percentage required for $Ir(C_{13}H_{10}N_3OS)_3$:

Ir = 20.0, N = 13.12, S = 10.0

Gravimetric Determination of Iridium :

Iridium was quantitatively precipitated with PBT from solutions adjusted to *p*H ranging from 4.2 to 5.86, and the required reagent concentration in the supernatant liquid for complete precipitation of the metal was 0.01% (W/V).

Procedure : A known amount of solution containing 4.00-12.00 mg of iridium(III) was diluted to 150 ml in a beaker, heated to boiling and 8-10 ml of 1% solution of PBT in 30% acetic acid solution were added per 10 mg of the metal. The mixture was stirred for 10 minutes and the *p*H was slowly adjusted to 4.2-5.86 with 4(*N*) ammonia solution and dilute hydrochloric acid. The mixture was again heated and stirred for 15 minutes when the orange yellow iridium complex was precipitated. The beaker with its contents was allowed to stand for 5 hours on boiling water bath with occasional stirring. The complex was filtered through a sintered glass crucible (No. 4), washed with hot water, dried at 110°-115°, cooled in a desiccator and weighed as Ir $(C_{18}H_{10}N_2OS)_3$.

Effect of diverse ions :

Iridium was determined with PBT in different solutions containing a known amount of iridium(III) and the requisite amount of the base metal in presence of a suitable masking agent, by following the above procedure.

TABLE 1 – SEPARATION OF IRIDIUM FROM DIVERSE IONS

Iridium taken = 8.1 mg

Foreign ion added (mg)	Iridium found (mg)	Foreign ion added (mg)	Iridium found (mg)
Co^{2+}(200)[a]	8.08	UO_2^{2+} (200)[a]	8.1
Ni^{2+}(200)[a]	8.08	Th^{4+} (200)[a]	8.1
Mn^{2+}(200)[a]	8.1	V^{5+} (200)[a]	8.1
Zn^{2+}(500)[a]	8.12	Mo^{6+} (200)[a]	8.08
Cd^{2+}(200)[b]	8.1	W^{6+} (200)[a]	8.08
Hg^{2+}(100)[b]	8.12	Au^{3+} (50)[b]	8.1
Ga^{3+}(200)[a]	8.12	PO_4^{3-} (500)	8.08
In^{3+}(100)[a]	8.08	F^- (500)	8.08
Tl^{3+}(200)[a]	8.1	E.D.T.A^{2-} (1000)	8.1
Cu^{2+}(200)[b]	8.12	Pd^{2+} (23.6)	8-08
Fe^{3+}(200)[b]	8.12	Pt^{4+} (19.4)	8.1
Pb^{2+}(200)[b]	8.12	Ru^{3+} (21.8)	8.08
Ti^{4+}(100)[c]	8.08	Os^{6+} (29.4)	8.08

a – in presence of tartrate ions

b – in presence of E.D.T.A.

c – in presence of fluoride ions.

To separate iridium from palladium(II) or platinum(IV), the latter metal ions were first precipitated with PBT from 1.5(*N*) hydrochloric acid medium and filtered. Iridium was then determined in the filtrate with PBT. The interferences of ruthenium(III) and osmium(VI) were avoided by their prior reduction with hydroxylamine hydrochloride and sulphur dioxide respectively. Rhodium(III), however interferes. The results are recorded in Table 1.

Precision and accuracy : The relative standard deviation and relative mean error for the gravimetric determination of the metal with PBT were calculated and found to be 0.30% and 0.12% respectively.

Spectrophotometric Determination of Iridium :

The extraction of the iridium-PBT complex was found to be quantitative when the *p*H of the aqueous layer was maintained between 5.2 and 6.4. The iridium complex was completely extracted in chloroform and in isobutyl methyl ketone in presence of a few ml of ethanol. In benzene, nitrobenzene, ether and carbon-tetrachloride the complex was, however, only partially extracted.

Absorbance curves :

Absorbance curves of the extracts of iridium (III)-PBT complex in chloroform-ethanol mixture, containing varying concentrations of the metal are shown in fig. 1. The extracts show maximum absorbance at 350 nm and obey Beer's law at the same wavelength over the concentration range of iridium from 0.816 μg/ml to 8.16 μg/ml.

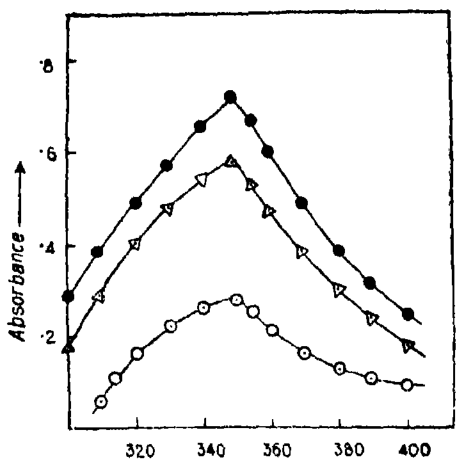


Fig. 1. Absorbance curves of iridium (III)-N-4-pyridyl-N'-benzoyl thiourea complex in chloroform-ethanol mixture [Ir III]: [○] = 2·46 μg/ml. [Δ] = 4·9 μg/ml [●] = 6·55 μg/ml

Procedure : A measured amount of standard iridium(III) solution was introduced in a 100-ml separatory funnel, adjusted to *p*H 5.2-6.4 by adding 10% sodium acetate solution and dilute hydrochloric acid, and 0.01 (*M*) ethanolic solution of PBT (about 10 times

the theoretical amount) was added. The separatory funnel with its contents was placed on a boiling water bath for about 45 minutes, cooled to room temperature, 5 ml of ethanol were added and mixed thoroughly. The iridium complex was then extracted 2-3 times with 5-ml portions of chloroform. The extracts were collected in a 25-ml volumetric flask and diluted to the mark with chloroform. The absorbance of the extract was measured at 350 nm against appropriate reagent blank, prepared under similar conditions.

Effect of diverse ions :

In the presence of large amounts of base metal ions, iridium was spectrophotometrically determined with PBT using a suitable masking agent like E.D.T.A., fluoride or tartrate ions. The metal was separated from palladium by preliminary extraction of the latter with PBT at *p*H 2.0. The interference of platinum(IV) was avoided by its prior extraction with PBT in 1.5 (*N*) hydrochloric acid. To avoid the interferences of ruthenium(III) and osmium(VI), preliminary reduction of these metal ions was carried out with hydroxylamine hydrochloride and sulphur dioxide respectively. The tolerance limits (i.e. the concentration of diverse ions causing an error less than ± 2% in the transmittance value) are recorded in Table 2.

TABLE 2—EFFECT OF DIVERSE IONS IN THE SPECTROPHOTOMETRIC DETERMINATION OF IRIDIUM

Iridium taken = 81.6 μg

Foreign ion added	Amount tolerated μg	Foreign ion added	Amount tolerated μg
Co^{2+}	3000[a]	Fe^{3+}	2000[b]
Ni^{2+}	2000[b]	UO_2^{2+}	5000[a]
Mn^{2+}	3000[a]	Th^{4+}	5000[a]
Cd^{2+}	2000[b]	Ti^{4+}	2000[c]
Hg^{2+}	500[b]	Pb^{2+}	2000
Ga^{3+}	1000[a]	Cu^{2+}	3000[b]
In^{3+}	1000[a]	Au^{3+}	500[b]
Tl^{3+}	1000[a]	Pd^{2+}	300
Mo^{6+}	500[a]	Pt^{4+}	300
W^{6}	500[a]	Ru^{3+}	250
V^{5+}	500[a]	Os^{8+}	250

a—In presence of tartrate ions
b—In presence of E.D.T.A. ions
c—In presence of fluoride ions

Nature of the complex in solution :

The empirical formula of the iridium(III)-PBT complex was determined by the mole-ratio method of Meyer and Ayres[13]. The results indicate that the molar ratio of the reagent to the metal ion in the iridium complex is 3:1. The results were verified by the slope-ratio method.

Molar absorptivity, Sensitivity, Precision and Accuracy :

The molar absorptivity of the iridium-PBT complex, the sensitivity of the colour reaction, the coefficient of variation and the relative mean error for the determination of the metal with PBT were found to be 1.8×10^4 l. mole^{-1}cm^{-1}, 0.01 μg cm^{-2}, 0.44% and 0.21% respectively.

Discussion

In the past attempts were made by various investigators to employ organic reagents for the gravimetry and spectrophotometry of iridium. The methods were, however, time consuming, requiring close control of the conditions of the reactions and the determination of the metal was interfered by commonly associated diverse ions. Moreover, none of these reagents formed any directly weighable complex with iridium. PBT offers a simple and rapid method for the gravimetric and spectrophotometric determination of iridium(III) with high accuracy. The most advantage of the use of PBT is that it can be applied in the gravimetric and spectrophotometric determination of iridium in the presence of large amounts of base metals and noble metals except rhodium(III).

Acknowledgement

The authors are indebted to the C.S.I.R. New Delhi, for awarding a fellowship to P.K.H.

References

1. R. NEEB, *Z. Analyt. Chem.*, 1960, **177**, 420.
2. R. R. BAREFOOT, W. J. McDONNEL and F. E. BEAMISH, *Analyt. Chem.*, 1951, **23**, 514.
3. N. LOMAKINA and I. P. ALIMARIN, *Zhur. Neorg. Khim.*, 1966, **11**(9), 2084.
4. A. D. WESTLAND and F. E. BEAMISH, *Analyt. Chem.*, 1955, **27**, 1776.
5. S. S. BERMAN, F. E. BEAMISH and W. A. E. McBRYDE, *Anal. Chim. Acta.*, 1956, **15**, 363.
6. R. NEEB, *Z. Analyt. Chem.*, 1957, **154**, 17.
7. G. S. MANKU, A. N. BHAT and B. D. JAIN, *Talanta*, 1969, **16**(10), 1421.
8. M. P. RAY, K. SUR and S. C. SHOME, *J. Indian Chem. Soc.*, 1974, **51**, 517.
9. D. K. DAS, M. MAZUMDAR and S. C. SHOME, *J. Indian Chem. Soc.*, 1977, **54**, 599.
10. S. C. SHOME, M. MAZUMDAR, P. K. HALDAR and D. K. DAS, *J. Indian Chem. Soc.*, 1977, **54**, 947.
11. D. K. DAS, M. MAZUMDAR and S. C. SHOME, *J. Indian Chem. Soc.*, 1977, **54**, 779.
12. P. K. HALDAR, M. MAZUMDAR and S. C. SHOME, *J. Indian Chem. Soc.*, 1977, **54**, 947.
13. A. S. MEYER and G. H. AYRES, *J. Amer. Chem. Soc.*, 1957, **79**, 49.

J. Indian Chem. Soc.,
Vol. LVII, February 1980, pp. 142-144

Studies on the Ternary Complexes of Vanadium(V) with N-Hydroxy-N-phenyl N'-o-chlorophenyl-p-Toluamidine Hydrochloride and Thiocyanate

(Miss) HEMLATA MOHABEY and RAJENDRA K. MISHRA*

Department of Chemistry, Ravishankar University, Raipur-492 010

Manuscript received 11 May 1979, accepted 23 December 1979

A spectrophotometric method for the determination of vanadium(V) based on the synergic extraction of ternary complex of vanadium with N-hydroxy-N-phenyl-N'-*o*-chlorophenyl-*p*-toluamidine hydrochloride (abbreviated as HPCPTH) and thiocyanate is reported. A 1.2.2 (metal : HPCPTH:$SC\bar{N}$) green complex in acidic medium is formed which can be extracted in chloroform. Beer's law is obeyed over the concentration of metal from 0 6 – 6 8 ppm. The molar absorptivity of the complex at 590 – 600 nm is about 6350 ± 50 l. mole^{-1} cm^{-1} and the Sandell's sensitivity is 0.008 μg of vanadium per cm^{-2}. The present mothod is simple, rapid and highly selective and most of the common ions including Mn^{2+}, Cr^{3+}, Ti^{4+}, Zr^{4+}, Mo^{6+} do not interfere. The applicability of this method has been tested by analysing three B.C.S. steels for vanadium.

N-hydroxy-N,N' diaryl benzamidines are reported as versatile reagents for carrying out determination of a large number of transition metal ions[1-5]. The newly synthesised hydroxyamidine-HPCPTH, monobasic and bidentate chelating agent reacts with vanadate ion giving blue-violet 1:2 complex having a flat peak in the region 550-580 nm. The addition of thiocyanate to this complex was found to produce a bathochromic shift in the wavelength of maximum absorption and a marked increase in the molar absorptivity. On the basis of the strong synergistic effect of thiocyanate and high molar absorptivity of the complex formed, a simple, rapid, sensitive and selective method is proposed for the extraction and spectrophotometric determination of vanadium(V) at microgram levels. The present method is superior to established methods[6-12].

Experimental

Apparatus : A Carlzeiss specord ultra-violet visible spectrophotometer with matched 1 cm. quartz and silica cuvettes was employed for recording the spectra. For all absorbance measurements an ECIL/VIS spectrophotometer model GS-865 was employed. The *p*H values of the solutions were measured with a systronic *p*H meter type-322.

Reagents : All the reagents used were of analytical purity.

A stock solution of ammonium meta vanadate was prepared by dissolving in doubly distilled water and standardised volumetrically using potassium permanganate[13]. From this stock solution, a solution containing 20 μg vanadium(V) ml^{-1} was prepared.

N-hydroxy-N-phenyl-N'-*o*-chlorophenyl-*p*-toluamidine hydrochloride was prepared following the method of Deb and Mishra[14]. The resulting hydrochloride was recrystallised from absolute ethanol. m.p. 168°, yield-75%. The compound gave satisfactory C, H and N analysis.

A 0.1% W/V solution of HPCPTH in chloroform was employed for extraction work. 5% aqueous potassium thiocyanate solution was used throughout the experiment.

Procedure : An aliquot of ammonium meta vanadate solution containing 100 μg of vanadium(V) is mixed with 2 ml of 5% potassium thiocyanate solution in a 100 ml separatory funnel. The total aqueous phase is made upto 25 ml. The *p*H of the solution is adjusted by dilute hydrochloric acid. Add 15 ml of reagent solution in chloroform and extract for 2 min, separate the coloured chloroform layer containing the vanadium(V) complex and collect over anhydrous sodium sulphate in a beaker. Extract the aqueous phase with 2×4 ml portions of chloroform. Transfer the combined extracts in 25 ml volumetric flask and dilute to volume with chloroform and measure the absorbance at λ_{max} of the complex.

Results and Discussion

Absorption spectra : The absorption spectra of vanadium(V)-HPCPTH-complexes in the absence and presence of thiocyanate are shown in figure 1. The vanadium(V)-HPCPTH complex shows a flat peak between 550-580 nm with molar absorbance 764 l.mole^{-1}cm^{-1}. In the presence of thiocyanate a stable

* Senior author

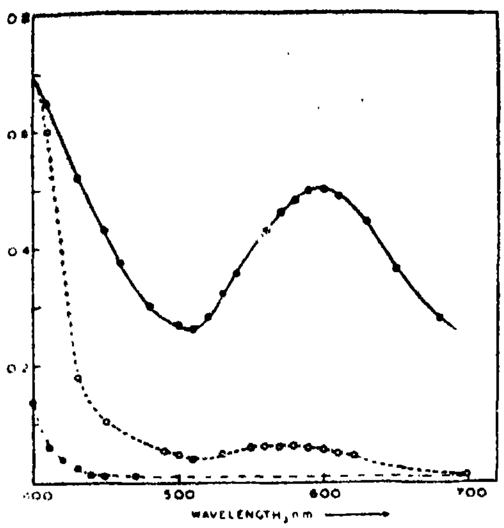


Fig. 1. Absorption spectra
(A) (–◐–◐–◐–◐–) V(V)-HPCPTH-SCN⁻
(B) (–○–○–○–○–) V(V)-HPCPTH
(C) (–●–●–●–●–) 0.1% W/V HPCPTH in chloroform.

1:2 green adduct is formed with molar absorptivity of about 6350±50 l.mole^{-1}cm^{-1} at 600 nm. A strong synergistic effect is observed as shown by the hyper and bathochromic shift on adduct formation.

Choice of solvent : Various water-insoluble organic solvents were tried. Benzene, toluene, carbontetrachloride and chloroform, all extracted the ternary complex. Chloroform proved to be most satisfactory because it gives high distribution ratio for the reagent and ternary complex.

Effect of variables : The optimum pH range is 0.8-3.0. Maximum absorption is reached when HPCPTH and thiocyanate concentration are 6 and 8 times that of vanadium respectively. Excess HPCPTH and thiocyanate cause no adverse effect on the λ_{max} and the absorbance value of the coloured system. The order of addition of reagents was not critical.

No adverse effect was noted on the absorbance of the coloured system when the ionic strength of the aqueous phase was adjusted between the 1-3 *M* potassium or sodium chloride. 2 min. was sufficient for complete extraction. The complex was stable for atleast 30 hr. at 27±2°.

Beer's law, optimum concentration range, molar absorptivity, sensitivity and precision :

The system obey's Beer's law within the concentration range of 0.6-8.0 ppm of vanadium(V). The effective working range from the Ringbom Plot[15-16] was found to be 1-5.8 ppm of vanadium(V). The sensitivity of the colour reaction is 0.008 μg/cm^2 at 600 nm with molar absorptivity 6350±50 l mole^{-1}cm^{-1}. The precision of the method has been checked by measuring the absorbance of 10 samples, each containing a final concentration of 4 ppm of vanadium(V). The mean absorbance was 0.50 with standard deviation 2.3×10^{-3}.

Composition : The composition of vanadium(V) : HPCPTH:SCN⁻ was determined by mole ratio[17], Job's method[18] and slope ratio[19] method. The result obtained showed the formation of 1:2:2 (metal:reagent: thiocyanate) mixed complex in chloroform.

Effect of Diverse ions : Many foreign ions were tested for interference with 4 ppm of vanadium(V) at 2.0±0.5 pH. The interference due to Fe^{3+} and Cu^{2+} could be eliminated by masking with *trisodium phosphate* and thiourea respectively. Chloride, bromide, iodide, nitrate, sulphate, thiosulphate, urea, thiourea, phthalate, borate, citrate, lanthanoid, tartrate, alkali and alkaline-earth metals did not interfere.

The tolerence limit for other ions are shown in Table 1.

TABLE 1—TOLERENCE LIMIT OF DIVERSE IONS IN THE DETERMINATION OF 4 PPM VANADIUM(V) AT 2.0±0.5 pH

Ions added	Tolerated* amount ppm	Ions added	Tolerated* amount ppm
Fe^{3+}	1000^a	Ti^{4+}	250
Co^{2+}	400	Mo^{6+}	150
Ni^{2+}	600	W^{6+}	10
Cu^{2+}	1600^b	Al^{3+}	900
Zn^{2+}	1000	Cr^{3+}	600
Cd^{2+}	1200	Th^{4+}	800
Mn^{2+}	600	Nb^{5+}	80
Be^{2+}	1500	Ta^{5+}	200
Zr^{4+}	150	F^-	500
Bi^{3+}	800	AsO_4^{3-}	400
U^{6+}	500	SeO_4^{2-}	800

* causing 2% error

a In presence of trisodium phosphate

b In presence of thiourea

Determination of vanadium in steel samples :

Steel samples containing upto 3 mg. of vanadium were dissolved in 40% nitric acid. Tungsten was removed as hydrated tungstic oxide by filtration. The filtrate was made upto 250 ml with distilled water and vanadium was determined by the procedure described above. Results are shown in Table 2.

TABLE 2—DETERMINATION OF VANADIUM(V) IN BCS* STEELS

Steel	Found / %	Certified value	Standard deviation
64a Alloy steel	1.56	1.57	0.0084
241/1 High speed steel	1.55	1.57	0.014
252 Low alloy steel	0.45	0.46	0.0070

* British Chemical Standard Bureau of Analysed Samples Ltd., Newham Hall, Middlesbrough, Yorks.

/ Mean of five results

Acknowledgement

The authors are thankful to Dr. S. G. Tandon, Head, Department of Chemistry, Ravishankar University, Raipur for providing research facilities. Award of Teacher fellowship to one of us (H.M.) by the U.G.C., New Delhi is gratefully acknowledged.

References

1. K. SATYANARAYANA and R. K. MISHRA, *Anal. Chem.*, 1974, 46, 1609.
2. K. SATYANARAYANA and R. K. MISHRA, *Indian J. Chem.*, 1975, 13, 295.
3. K. K. DEB and R. K. MISHRA, *Curr. Sci.*, 1976, 45, 134.
4. K. K. DEB and R. K. MISHRA, *J. Indian Chem. Soc.*, 1976, 53, 178.
5. K. S. PATEL and R. K. MISHRA, *Bull. Chem. Soc. Japan*, 1979, 52 595.
6. S. C. SHOME, *Analyst*, 1950, 75, 27.
7. D. E. RYAN, *Analyst*, 1960, 85, 569.
8. U. PRIYADARSHINI and S. G. TANDON, *Anal. Chem.*, 1961, 35, 435.
9. A. K. MAJUMDAR, N-benzophenyl hydroxylamine and its analogous, Pergamon, Oxford, 1972.
10. A. D. SHENDRIKAR, *Talanta*, 1969, 16, 51.
11. H. GOTO and Y. KAKITA, *Burseki Kagaku*, 1961, 10, 904.
12. O. A. VITA, W. A. LEVIER and E. LITTERAL, *Anal. Chim. Acta.*, 1968, 42, 37.
13. G. CHARLOT and D. BEZIER, Quantitative Inorganic Analysis, Wiley, New York, 1957.
14. K. K. DEB and R. K. MISHRA, *J. Indian Chem. Soc.*, 1976, 53, 178.
15. G. H AYRES, *Anal. Chem*, 1949, 21, 652.
16. A. RINGBOM, *Z. Anal. Chem.*, 1938, 115, 332.
17. J. H. YOE and A. L. JONES, *Ind. Eng. Chem. Anal. Ed.*, 1944, 16, 111.
18. P. JOB. *Ann. Chim. Paris*, 1928, 9, 113.
19. A. E. HARVEY and D. L. MANNING, *J. Amer. Chem. Soc* 1950, 72, 4488.

J. Indian Chem. Soc.,
Vol. LVII, February 1980, pp. 145-148

Studies on the Application of 2-hydroxy-4'-sulpho diazonaphthalene (FRA dye) used as an Adsorption Indicator in Argentometry

D. C. AGARWAL and G. K. CHATURVEDI

Chemical Laboratories, Agra College, Agra (India)

Manuscript received 6 September 1979, accepted 30 November 1979

2-hydroxy-4' sulpho diazonaphthalene (FRA dye) has been used as an adsorption indicator in direct or reverse titrations of silver ion with thiocyanate, chloride, bromide or iodide at pH 4-5.5. The silver compound of FRA dye has been isolated. Its behaviour and reactions provide suitable explanation for the color change in the argentometric titration carried out.

A number of dyes have been employed as an adsorption indicator in argentometry by Mehrotra and co-workers[1], Fajan *et al*[2]., Piazza *et al*[3]., Berry *et al*[4]., Tandon *et al*[5]., Koltboff *et al*[6]. and several others. Tandon *et al*[7]. described the use of benzene azo-1-naphthylamine as an adsorption indicator in the argentometric titrations.

In the present communication, 2-hydroxy-4'-sulpho diazonaphthalene (FRA dye) has been used as an adsorption indicator in the argentometric titration of halides and thiocyanate.

Experimental

Materials :

(i) NaCl, KBr, KI and $AgNO_3$ used were of A. R. grade. The stock solutions of these materials were prepared in double distilled water by direct weighing. The KSCN solution was standardised by usual method.

(ii) FRA dye was obtained from England through B. D. H. Bombay. 0.1% solution of the dye was prepared in double distilled water and kept in a stoppered container.

TABLE 1—HALIDE SOLUTION TAKEN = 50 ml, CONC. HALIDE SOLUTION = 0.001 *M* (HALIDE = KI, KBr, NaCl OR KSCN), CONC. Ag^+ = 0.01 *M*

% Eqvt. of Ag^+ added	pH changes											
	I^-			Br^-			Cl^-			SCN^-		
	I	II	III	I	II	III	I	II	III	I	II	III
0	4.22	4.75	5.29	4.22	4.60	5.20	4.20	4.75	5.25	4.74	5.24	5.57
20	4.28	4.80	5.34	4.23	4.62	5.26	4.22	4.78	5.50	4.76	5.31	5.62
40	4.30	4.90	5.42	4.24	4.64	5.31	4.23	4.80	5.58	4.79	5.38	5.70
60	4.32	5.00	5.50	4.27	4.67	5.39	4.24	4.83	5.68	4.84	5.42	5.77
80	4.37	5.10	5.63	4.28	4.69	5.43	4.25	4.87	5.78	4.88	5.48	5.81
90	4.39	5.19	5.75	4.29	4.70	5.46	4.26	4.88	5.86	4.90	5.52	5.85
95	4.41	5.22	5.79	4.29	4.72	5.49	4.27	4.90	5.88	4.90	5.54	5.86
100	4.41	5.22	5.79	4.30	4.72	5.49	4.27	4.90	5.88	4.90	5.54	5.86
105	4.43	5.23	5.80	4.31	4.77	5.51	4.28	4.91	5.89	4.93	5.57	5.88
110	4.46	5.25	5.81	4.34	4.79	5.53	4.29	4.92	5.90	4.95	5.59	5.91
120	4.50	5.29	5.83	4.36	4.80	5.54	4.30	4.93	5.91	4.97	5.62	5.95
140	4.60	5.34	5.88	4.38	4.82	5.57	4.31	4.95	5.92	4.99	5.64	6.01
160	4.76	5.40	5.93	4.40	4.85	5.61	4.32	4.96	5.93	5.01	5.65	6.05

TABLE 2—FRA DYE AS ADSORPTION INDICATOR IN THE TITRATION OF HALIDE OR THIOCYANATE ION

Vol. and conc. of halide or thiocyanate	Indicator drops	Vol. and Conc. of $AgNO_3$	Transition at Eqvt. point	Detailed conditions
10.0 ml of M/10 NaCl+ (1 ml of 0.01 *M* HNO_3)	4	10.00 – 10.05 ml of M/10 $AgNO_3$	Red Susp. →violet pink ppt.	Coagulation just before the end point. Color change sharp and reversible
10.0 ml of M/10 KBr+ (1 ml of 0.01 *M* HNO_3)	3	9.95 – 10.00 ml of M/10 $AgNO_3$	,,	Coagulation much earlier and color change sharp and reversible
10.0 ml of M/10 KI+ (1 ml of 0.01 *M* HNO_3)	2	10.00 – 10.05 ml of M/10 $AgNO_3$	Red Susp. →light violet pink ppt.	Color change on the coagulated precipitate, sharp and reversible
10.0 ml of M/10 KSCN+ (1 ml of 0.01 *M* HNO_3)	4	9.95 – 10.00 ml of M/10 $AgNO_3$	Red Susp. →violet pink ppt.	Coagulation much earlier but color change at the equivalence point was not as sharp as in above
10.0 ml of M/50 NaCl+ (2 ml of 0.01 *M* HNO_3)	4	10.05 ml of M/50 A NO_3	Red Susp. →violet pink ppt.	Color change on the coagulated precipitate, sharp and reversible
10.0 ml of M/50 KBr+ (ml of 0.01 *M* HNO_3)	4	9.95-10.00 ml of M/50 $AgNO_3$	Red Susp. →violet pink ppt.	,, ,,
10.0 ml of M/50 KI+ (ml of 0.01 *M* HNO_3	4	10.00 – 10.05 ml of M/50 $AgNO_3$	Red Susp. →violet pink ppt.	,, ,,
10.0 of M/50 KSCN+ (1 ml of 0.01 *M* HNO_3)	4	9.95 – 10 00 ml of M/50 $AgNO_3$	Red Susp. →violet pink ppt.	Color change not sharp as in above
10.0 ml of M/100 NaCl+ (2-3 ml of 0.01 *M* HNO_3)	4	10.05 – 10.00 ml of M/100 $AgNO_3$	Red Susp. →Violet pink ppt.	Color change on the coagulated precipitate, sharp and reversible
10.0 ml of M/100 KBr+ (2-3 ml of 0.01 *M* HNO_3)	4	10.00 – 10.05 ml of M/100 $AgNO_3$	Red Susp. →Violet pink ppt.	,, ,,
10.0 ml of M/100 KI+ (2-3 ml of 0.01 *M* HNO_3)	3	9.95 – 10.00 ml of M/100 $AgNO_3$	Red Susp. →Violet pink ppt.	,, ,,
10.0 ml of M/100 KSCN+ (2-3 ml of 0.01 *M* HNO_3)	4	10 00 – 10.05 ml of M/100 $AgNO_3$	Red Susp. →Violet pink ppt.	Color change in suspension phase and not sharp
10.0 ml of M/200 NaCl+ (2-5 ml of 0.01 *M* HNO_3)	2	10.00 – 10.05 ml of M/200 $AgNO_3$	Red Susp. →Violet pink susp.	Equivalence point in the suspension phase, sharp and reversible
10.0 ml of M/200 KBr+ (2-5 ml of 0.01 *M* HNO_3)	2	10.00 – 10.05 ml of M/200 $AgNO_3$	Red Susp. →Violet pink susp.	,, ,,
10.0 ml of M/200 KI+ (2-5 ml of 0.01 *M* HNO_3)	2	9.95 – 10.00 ml of M/200 $AgNO_3$	Red Susp. →Violet pink susp.	Color change on the coagulated precipitate, sharp and reversible
10.0 ml of M/500 KI+ (3-5 ml of 0.01 *M* HNO_3)	2	10.00 – 10.05 ml of M/500 $AgNO_3$	Red Susp. →Violet pink susp.	Color change in suspension, sharp and reversible

***Method*:**

The FRA dye shows a sharp color change from red to violet pink in the *p*H range 4-5.5. In this *p*H range halides can be titrated with silver ions with a sharp color change of the AgX (which is also reversible) or AgSCN at the equivalence point. The violet-pink color of the suspension or precipitate of AgX (where X=Cl, Br and I) or AgSCN changes to violet on standing in sunlight for long. The sharpness in color change

during argentometric titration decreases in the order $I^- > Br^- > Cl^- > SCN^-$. The titration with silver ions could be satisfactorily carried out in the solution with dilution 0.002 *M* (in case of iodide), 0.005 *M* (in case of bromide and chloride) and 0.01 *M* (in case of thiocyanate).

color change occurred simultaneously and instantaneously.

In the reverse titration the coagulation occurred much earlier and the dye was adsorbed completely changing the color of the precipitate to violet pink. However, at

TABLE 3—FRA DYE AS ADSORPTION INDICATOR IN THE TITRATION OF Ag^+ IONS WITH HALIDS OR THIOCYANATE (INDICATOR DROPS—4)

Vol. and Conc. of $AgNO_3$	Vol. and Conc. of halide or thiocyanate	Transition at the equivalence point	Detailed conditions
10.0 ml of M/10 $AgNO_3$	9.95-10.05 ml of M/10 NaCl	Violet pink ppt. → Red suspension	Coagulation much earlier and dye absorbed on the coagulated precipitated, but at the equivalence point adesorption of the dye and red colour comes in the supernatent liquid. End point sharp and reversible.
10.0 ml of M/10 $AgNO_3$	10.00-10.05 ml of M/10 KBr	,, ,,	
10.0 ml of M/10 $AgNO_3$	9.95-10.00 ml of M/10KI	,, ,,	
10.0 ml of M/10 $AgNO_3$	10.00 ml of M/10KSCN	,, ,,	
10.0 ml of M/50 $AgNO_3$	9.95-10.00 ml of M/50 NaCl	,, ,,	Desorption of the dye exectly at the equivalence point, sharp & reversible.
10.0 ml of M/50 $AgNO_3$	10.00-10.05 ml of M/50 KBr	,, ,,	
10.0 ml of M/50 $AgNO_3$	9.95-10.00 ml of M/50 KI	,, ,,	
10.0 ml of M/50 $AgNO_3$	9.95-10.00 ml of M/50 KSCN	,, ,,	
10.0 ml of M/100 $AgNO_3$	9.95-10.00 ml of M/100 NaCl	,, ,,	Coagulation near the equivalence point and desorption of the end point, sharp and reversible. End point not sharp in the case of KSCN.
10.0 ml of M/100 $AgNO_3$	9.95-10.00 ml of M/100 KBr	,, ,,	
10.0 ml of M/100 $AgNO_3$	10.00-10.05 ml of M/100 KI	,, ,,	
10.0 ml of M/100 $AgNO_3$	9.95-10.00 ml of M/100 KSCN	,, ,,	

pH changes during titration :

To 50 ml solution of 0.001 *M* halides, 10 drops of dye indicator solution was added and solution titrated against 0.01 *M* $AgNO_3$ solution. The initial *p*H was adjusted by adding 0.01 *M* HNO_3 or 0.01 *M* NaOH or NH_4OH, according to the halide ions titrated (Table 1). Every titration was repeated thrice in order to get reproducibility. The *p*H measurements were carried out using Philips *p*H-meter (PR 9405 *M*). The *p*H of the medium at equivalence point was found out by these studies.

Titration of halide or thiocyanate with $AgNO_3$ and vice versa :

10.0 ml of halide or thiocyanate solution was taken and the *p*H of the solution was adjusted in the range (4-5.5) by adding the required drops (1-5 ml) of 0.01 *M* HNO_3. 2-4 drops of dye solution was added and the solution was titrated against standard $AgNO_3$ solution.

At the equivalence point white precipitate of AgX or AgSCN acquired a violet pink color. In more dilute solution the complete coagulation of the precipitate and the equivalence point desorption of the dye took place giving supernatant solution a red color. The observations are recorded in Tables 2 and 3.

Preparation of the silver dye compound :

About 0.30 gm of the FRA dye was dissolved in 30-40 ml of ether and 10 ml of alcohol. It was shaken with few drops (5-6) of 1 *M* HNO_3 acid and 5 ml of 20% $AgNO_3$ solution. The reddish orange precipitate was formed in the ethereal layer which was separated and filtered. The silver-dye compound was dried in a desiccator over prorous plate for 2-3 days.

The silver-dye complex obtained is not stable in bulk, it gets hydrolysed in aqueous medium but is quite stable in ether. In aqueous medium in the presence of few drops of HNO_3, halide and SCN^- ions give a violet pink precipitate identical to that observed during the argentometric titration of these anions using the above indicator.

The Ag-Dye derivative formed, was analysed for Ag by dissolving it in concentrated HNO_3 and precipitating Ag^+ as AgCl which was filtered, dried and weighed. The results are recorded in table 4.

TABLE 4

Wt. of Ag-Dye complex (mg)	Wt. of AgCl obtained (mg)	Wt. of Ag^+ in the AgCl (mg)	Theoretical amount of Ag^+ calculated (mg)
250	73.4	55.24	55.58
350	102	76.76	77.82
450	130.6	98.30	100.05

Discussion

The color changes during argentometric titration of the halide and thiocyanate ions using FRA dye can be explained on the basis of the view of Schulek and Pungor[8]. First the particle of AgX (X=Cl, Br and I) or AgSCN probably adsorb positively charged Ag^+ ion on its surface. The dye react with the precipitate forming a violet pink Ag-dye compound at the equivalence point. AgX or AgSCN having low solubility product is precipitated first. Just before the end point (when practically all X^- or SCN^- ion are converted in their Ag compounds) is reached, the Ag-dye complex having higher solubility product starts forming at the surface of the precipitate giving it a violet pink color. The mechanism may be expressed as follows :

$$\underset{\text{White ppt}}{(AgX)}\ \underset{\text{red}}{Ag^+ + Dye} \xrightarrow{\text{at the end point}} \underset{\text{violet pink}}{(AgX)\ Ag\text{-}Dye}$$

The studies indicate that the *p*H of the medium remains almost constant near the equivalent point at *p*H (4 to 5.5) and the coagulation of the precipitate is instantaneous at the equivalence point.

Acknowledgement

The authors express their grateful thanks to Prof. J. P. Tandon, Head of Chemistry Department, University of Rajasthan, Jaipur, for his valuable suggestions. Thanks are also due to Dr. S. M. L. Gupta, Head of Chemistry Department, Agra College, Agra, for providing necessary laboratory facilities.

References

1. R. C. MEHROTRA, R.D. TEWARI and H.L. DUBE, *J. Indian Chem. Soc.*, 1947, **24**, 165.
2. K. FAJAN and H. WOLFF, *Z. anorg. Chem.*, 1924, 137, 221.
3. G. PIAZZA and L. BALLADEN, *Ann. Chim. appl.*, 1932, 22, 631.
4. A. J. BERRY and P. J. DURRANT, *Analyst*, 1936, 61, 315.
5. K. N. TANDON and R. C. MEHROTRA, *Anal. Chim. Acta*, 1962, 27, 15-19.
6. I. M. KOLTHOFF, *Z. anal. Chem.*, 1927, 70, 395.
7. K. N. TANDON and R. C. MEHROTRA, *Anal. Chim. Acta*, 1962, 27, 97.
8. E. SCHULEK and E. PUNGOR, *Anal. Chim. Acta*, 1950, 4, 213.

J. Indian Chem. Soc.,
Vol. LVII, February 1980, pp. 149-151

Kinetics of Oxidation of α-Amino Acids by Periodate

M. PRASADA RAO, B. SETHURAM and T. NAVANEETH RAO

Department of Chemistry, Osmania University, Hyderabad-500 007

Manuscript received 26 May 1977, revised 3 March 1979, accepted 30 December 1979

Kinetics of oxidation of α-amino acids viz. glycine, alanine, phenylalanine, glutamic acid and aspartic acid by periodate has been studied in aqueous medium with a view to find out the behaviour of the periodate, which is a specific oxidant for 1,2-glycols. The order in [amino acid] and [periodate] were found to be one each and the overall reaction followed second order kinetics. The rates decreased with increase in $[H^+]$. Addition of salts like KCl, $NaNO_3$ and $NaClO_4$ had negligible effect on the rates. The products of oxidation were identified as the corresponding aldehydes apart from CO_2 and NH_3. A mechanism similar to that observed in the oxidation of 1,2-glycols is proposed to explain the results. Activation parameters are also presented and discussed.

PERIODATE has been used as a selective oxidizing agent for the cleavage of 1,2-glycols[1], α-hydroxy acids[2], 1,2-diketones[3], amino alcohols[4] and other organic substrates[5]. Clamp *et al*[6] suggested that oxidation of glycine and N-substituted glycines proceed by an electrophilic attack of the oxidant on nitrogen giving an intermediate complex which decomposes to products via the imino compound. As no detailed kinetic investigation has so far been attemped it was thought worth while to study the kinetics of oxidation of some α-amino acids by periodate to get a clear picture of the mechanism.

Experimental

All the chemicals used were of BDH (AR) grade and purified wherever necessary by standard methods. KOH and HOAc solutions in different proportions were used for the variation of *p*H. KCl was used for adjusting the ionic strength. The rate of the reaction was followed iodometrically[7] and the concentration of periodate at any time was calculated by making allowance for the reductionof IO_3^-. The products of oxidation were CO_2, NH_3 and the corresponding aldehydes and these were detected by their characteristic tests[5].

Results and Discussion

The reaction followed second order kinetics (Table-1) with first order dependence on each of the reactants. The rate of oxidation increased with increase in *p*H (Table-2) for all amino acids except in the case of glutamic and aspartic acids where a rate maxima was observed at *p*H 4.5 and 7 respectively. This may be due to the existance of different periodate species formed probably by the dissociation of the main species viz H_5IO_6[8a,b]. According to the equilibrium proposed by Crouthamel and coworkers[9]

$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+ \quad \text{— (1)}$$

TABLE 1—DEPENDENCE OF RATE ON THE [AMINO ACID] AND $[KIO_4]$

$\mu = 0.008\ M$; *p*H = 6.5 ; Temperature = 324 K

Glycine mol.lit^{-1}	$[KIO_4]\times10^3$ mol. lit^{-1}	$k'\times10^3$ min^{-1}	$k'/[A.A]\times10^3$ lit mol.$^{-1}$ min^{-1}
0.100	0.400	2.95	—
0.100	0.800	3.05	30.5
0.200	0.800	6.56	32.8
0.300	0.800	9.20	30.7
0.400	0.800	13.8	34.6
0.500	0.800	17.3	34.6
0.600	0.800	21.2	35.3
0.750	0.800	26.2	34.9

if $H_4IO_6^-$ were to be the reactive species, increase in $[H^+]$ should decrease the rate. Such a trend was observed (Table-2) in the present work suggesting $H_4IO_6^-$ to be the reactive species. From the oxidation studies of glycols[10] Buist and Bunton suggested that a uninegatively charged complex in its dehydrated form splits readily into products and that the undissociated (H_5IO_6) or dinegatively charged ($H_3IO_6^{2-}$) complexes are inert. The effect of added salts viz. KCl, $NaNO_3$ and $NaClO_4$ (0.050—0.450*M*) was found to be negligible indicating the reaction to be an ion-dipole type one. The intermediate complex suggested by earlier workers in the oxidation of other organic substrates could not be detected kinetically in the present work as the plot of $1/k'$ vs $1/[A.A]$ was linear (fig-1) with no intercept. A mechanism involving the formation of an unstable intermediate in a slow rate determining step by the electrophilic attack on nitrogen

TABLE 2—VARIATION OF RATE WITH pH

$[KIO_4^-]=0.005\ M$; Temperature=323 K.

		pH 10.2	9.60	9.00	8.60	7.10	6.20	5.10	4.50	4.20	3.00
$k' \times 10^{3}$ min^{-1}	gly.	—	6.68	3.45	2.30	—	0.500	0.380	—	0.320	0.265
	glu.	1.57	—	1.62	1.68	1.72	—	1.89	2.07	1.96	1.54
	asp.	2.60	—	4.20	4.61	5.61	—	4.25	3.68	3.40	2.15

gly.=glycine=0.200 M ; glu.=glutamic acid=0.040M ; asp.=aspartic acid=0.040M.

by periodate is proposed to explain the oxidation. This intermediate cyclizes and undergoes C-C bond fission giving rise to products via the imino compound (Chart-1).

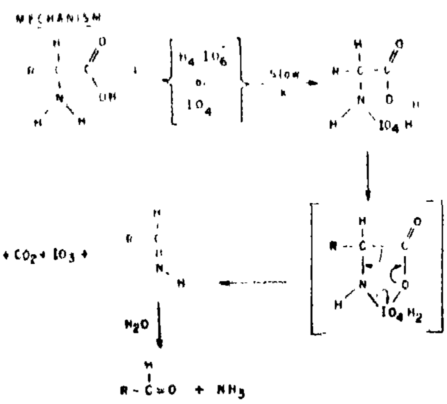


Chart 1

The observed rate law may be written as follows :

$$-\frac{d[P]_t}{dt}=k''[P]_t\,[A.A] \qquad \ldots (2)$$

where $[P]_t$ = Concentration of total periodate species $=[H_5IO_6]+[H_4IO_6^-+IO_4^-]+[H_3IO_6^{2-}]+[H_2IO_6^{3-}]$

and [A.A.]=Concentration of amino acid.

It has been shown by earlier workers[8] that in the pH range 4–10 the most likely reactive species are $H_4IO_6^-$, IO_4^- and $H_3IO_6^{2-}$. Therefore the rate expression for the reaction in this pH range may be written as

$$\left.\begin{array}{l} H_4IO_6^- \\ IO_4^- \\ H_3IO_6^{2-} \end{array}\right| + A.A. \xrightarrow{k} \text{products}$$

$$-\frac{d[P]_t}{dt}=\{k_1[H_4IO_6^-+IO_4^-]+k_2[H_3IO_6^{2-}]\}[A.A.] \ldots (3)$$

where k_1 and k_2 are the rate coefficients for the reaction of mononegatively and dinegatively charged species with A.A. respectively.

Equating (2) and (3)

$$k''[P]_t\,[A.A]=\{k_1[H_4IO_6^-+IO_4^-]+k_2[H_3IO_6^{2-}]\}[A.A] \quad \ldots (4)$$

$$\text{or}\quad k''=k_1/x_1+k_2/x_2 \qquad \ldots (5)$$

where x_1 and x_2 are the correction terms for the availability of the periodate species and can be expressed as follows :

$$x_1=1+\frac{\bar{K}_2\,.\,f^-}{f^{2-}\,.\,a_{H^+}}$$

$$x_2=1+\frac{f^{2-}\,.\,a_{H^+}}{\bar{K}_2\,.\,f^-}$$

where $\bar{K}_2$ = apparent second ionisation constant of periodate species[11] and can be expressed as

$$\bar{K}_2=\frac{[H_3IO_6^{2-}]f^{2-}\,.\,a_{H^+}}{[H_4IO_6^-+IO_4^-]f^-}$$

where,

a_{H^+} is hydrogen ion activity obtained from pH measurements.

f^- and f^{2-} are activity coefficients of mono and dianion of periodate species (calculated from Devies' equation[12]).

The values of k_1 and k_2' for glycine calculated from the experimental k'' values are as follows :

$k_1=(1.25\times10^{-4}$ to $1.38\times10^{-4})$ lit. mol^{-1} sec.$^{-1}$ and $k_2=(1.29\times10^{-3}$ to $0.93\times10^{-3})$ lit. mol^{-1} sec^{-1}.

The marked increase in the rate of oxidation above pH 7 in the case of glycine, alanine and phenylalanine could be explained by assuming the cyclization of the monoester to be base catalysed similar to the observations made by Buist and Bunton in the pinacol oxidation[13]. The hydroxyl ion acting as a powerful catalyst compared to water in the basic medium, releases the proton of the hydroxyl group thereby favouring cyclization (Chart-2).

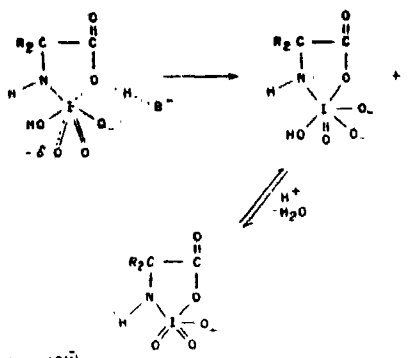


Chart 2

In the case of glutamic and aspartic acids a rate maximum appears at pH 4.5 and 7, respectively. The rate maxima at these pH values are to be expected because periodate monoanions exist predominantly[9] only in the pH range 3-7. It is likely that the base catalysis is suppressed in the case of more acidic amino acids due to the presence of additional carboxylic acid groups present in the molecule. The rate maximum at higher pH for aspartic acid may be due to its lower pK_1 and pK_2 values compared to glutamic acid.

The order of the rates of oxidation is phenylalanine > aspartic acid > glutamic acid > glycine > alanine. Thus it is clear that the rates of oxidation increase as the pK_a values decrease or the dissociation of the amino acids increases (Table-3). Activation

TABLE 3—SECOND ORDER RATE CONSTANTS AND ACTIVATION PARAMETERS AT 338 K

Amino acid	pK_a of the A.A.	$k'' \times 10^3$ lit mol⁻¹ sec⁻¹	$\Delta E^{\ddagger}$ (k cals mol⁻¹)	$\Delta H^{\ddagger}$ (k cals mol⁻¹)	$\Delta G^{\ddagger}$ (k cals mol⁻¹)	$-\Delta S^{\ddagger}$ e.u.
glycine	2.34	2.50	19.1	18.4	23.9	16.3
alanine	2.34	1.80	18.8	18.1	24.1	17.8
phenylalanine	1.83	11.9	21.5	20.8	22.9	6.00
aspartic acid	1.88	3.40	13.1	12.4	23.7	33.4
glutamic acid	2.19	2.70	16.2	15.5	23.9	24.6

parameters have been calculated and are listed in the Table 3. The high $\Delta S^{\ddagger}$ value in case of phenylalanine is indicative of a less rigid activated complex. A plot of $\Delta H^{\ddagger}$ vs $\Delta S^{\ddagger}$ was linear (Fig. 1) indicating that

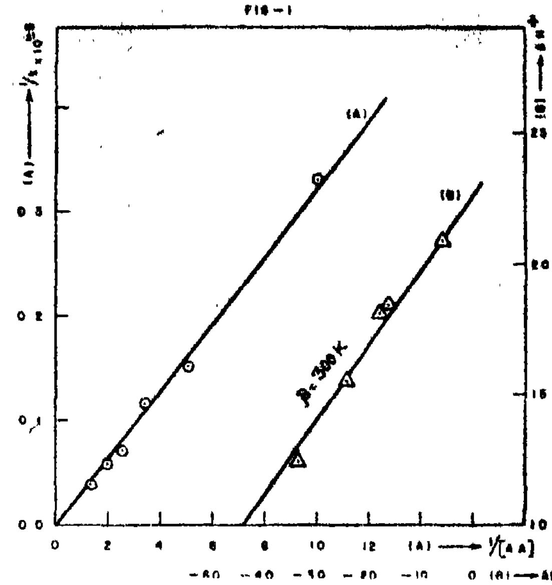


Fig. 1. (A) $1/k' \times 10^{-3}$ vs $1/[A.A.]$ Temp. = 324 K ; μ = 0.008 M ; pH = 6.5 (B) $\Delta H^{\ddagger}$ vs $\Delta S^{\ddagger}$

this reaction series follows isokinetic phenomena[14]. The isokinetic temperature (β) was found to be 300°K which is decidedly lower than the experimental temperature range (323-338°K) used suggesting that the reactions are entropy controlled.

References

1. G. J. BUIST and C. A. BUNTON, *J. Chem. Soc.*, 1957, 4567.
2. S. D. PAUL and D. G. PRADHAN, *Indian J. Chem.*, 1073, 11, 1155.
3. V. J. SHINER and C. R. WASMUTH, *J. Amer. Chem. Soc.*, 1959, 81, 37.
4. GEORGE DAHLGREM and M. JOHN HODSON, *J. Phys. Chem.*, 1964, 68 (2), 416.
5. B. P. YADAVA and HARIKRISHNA, *Indian J. Chem.*, 1968, 6, 514.
6. J. R. CLAMP and L. HOUGH, *Biochem. J.*, 1966, 101, 120.
7. PERLIN, '*Oxidation Techniques and Applications in Organic Synthesis*', Vol. I edited by R.L. AUGUSTINE (Marcel Dekker Inc., N. Y.), 1969, p. 199.
8. F. FEIGL, '*Spot Tests in Organic Analysis*' Elsevier Publishing Company, Amsterdam, 1966, p. 195.
9. a) C. E. CROUTHAMEL, H. V. MEEK, D. S. MARTIN and C. V. BANKS, *J. Amer. Chem. Soc.*, 1949, 71, 3031.
   b) C. E. CROUTHAMEL, A. M. HAYES and D. S. MARTIN, *J. Amer. Chem. Soc.*, 1951, 73, 82.
10. G. J. BUIST and C. A. BUNTON, *J. Chem. Soc.*, 1954, 1406.
11. G. J. BUIST, W. C. P. HIPPERSON and J. D. LEWIS, *J. Chem. Soc.*, A, 1969, 307.
12. C. W. DAVIES, '*Ion Association*', Butterworths, London, 1962, p. 41
13. G. J. BUIST, C. A. BUNTON and J. LOMAS, *J. Chem. Soc.*, B, 1966, 1099.
14. J. E. LEFFLER, *J. Org. Chem.*, 1955, 20, 1202.

J. Indian Chem. Soc.,
Vol. LVII, February 1980, pp. 152-154

Kinetics and Mechanism of Oxidation of Arsenic(III) by Chloramine-T*

G. BABU RAO, A. KODANDA RAMAIAH and P. V. KRISHNA RAO**

Department of Chemistry, Andhra University, Waltair

Manuscript received 21 February 1979, revised 21 November 1979, accepted 31 December 1979

The kinetics of oxidation of arsenic (III) by chloramine-T has been studied in an alkaline medium. The reaction is first order both in the substrate and in the oxidant. An inverse first order dependence on $[OH^-]$ has been observed. The effect of varying the ionic strength on the reaction rate is found to be negligible. A decrease in the dielectric constant of the medium increases the rate. The energy and entropy of activation for the oxidation process are 42.7 KJ mol^{-1} and -109.3 JK^{-1} (at 273°K) respectively. The proposed mechanism involves an interaction between $AsO(OH)_2^-$ ion and *p*-toluene sulphochloramide in the rate determining step.

ALTHOUGH the oxidation kinetics of many organic compounds by Chloramine-T(CAT) have been studied extensively[1], similar studies on inorganic compounds are rather scanty. Mushran and coworkers[2] have reported the oxidation kinetics of hexacyanoferrate(II) by CAT. In the present communication, the results of our kinetic study on the oxidation of arsenic(III) by CAT are reported. Kinetic studies on the oxidation of arsenic(III) by some oxidising agents have been reported[3-7] in the literature.

Experimental

Reagents : E. Merck (p.a) sample of CAT was used without purification. Aqueous solutions of appropriate strength were prepared and stored in black-coated bottles. The strength of the aqueous solution was ascertained by the iodometric method[8].

Aqueous solution of sodium arsenite was prepared by dissolving an accurately weighed sample of arsenoius oxide (A.R,B.D.H) in 1.0 *N* sodium hydroxide and finally neutralising the excess alkali by 1.0*N* hydrochloric acid.

All other reagents were of acceptable grade purity. Methanol was purified by distilling twice. The reaction vessels were coated black to exclude photochemical effects.

Kinetic measurements : Requisite amounts of arsenic(III) and sodium hydroxide solutions were taken in a reaction vessel and were thermostated in an Ultra Cryostat (Remi, RK 701) maintained at O°. The reaction was initiated by adding a measured aliquot of CAT which was also pre-thermostated to the same temperature. The progress of the reaction was followed by estimating the unreacted CAT iodometrically at various time intervals. The pseudo-first order rate constants(k_1) were calculated from the slopes of plots of log [CAT] versus time which were reproducible within ±4%.

Results

Stoichiometry : Reaction mixtures containing excess CAT over arsenic(III) and vice-versa were kept at 30° in the presence of sodium hydroxide ($4.0\times10^{-3}M$) for 48 hours. An estimation of the unreacted CAT or arsenic(III) has shown that, in either case, one mole of arsenic(III) consumed one mole of CAT which is in accordance with the earlier reports[9].

Effect of reactant concentration : Kinetic runs were carried out at different initial concentrations of the reactants (Table 1). The reaction is first order in CAT

TABLE 1—EFFECT OF REACTANT CONCENTRATIONS

$[NaOH]=4.0\times10^{-3}M$, Temp: 0°C.

$[CAT]\times10^4M$	$[As(III)]\times10^3M$	$k_1\times10^4s^{-1}$.
5.0	5.0	10.53
7.5	10.0	21.40
10.0	10.0	21.80
5.0	6.25	13.75
5.0	7.50	16.23
5.0	8.75	19.25
5.0	10.0	21.66
5.0	11.25	24.75
5.0	12.50	27.59

*Presented at the Annual Convention of Chemists (1978), Waltair.
**for correspondence.

as is evident from the linearity of plots of log [CAT] versus time. The first order dependence in CAT is further confirmed by the constancy of the k_1 values at different initial [CAT]. The k_1 values were proportional to [As(III)] at different initial [As(III)]. A plot of k_1 against [As(III)] gives a straight line passing through the origin thus indicating the first order dependence on [As(III)].

Effect of $[OH^-]$: The rate of the reaction decreases with an increase in $[OH^-]$ (Table 2). The slope of the plot of $\log(k_1)$ versus $\log [OH^-]$ is nearly unity indicating an inverse first order dependence of the rate on $[OH^-]$.

TABLE 2—EFFECT OF ALKALI CONCENTRATION

[As(III)]=$5.0\times10^{-3}M$., [CAT]=$5.0\times10^{-4}M$, Temp : 0°C.

$[NaOH]\times10^3M$	4.0	5.0	6.0	7.0	8.0
$k_1\times10^4s^{-1}$	10.53	7.83	6.42	5.30	4.73

Effect of ionic strength and dielectric constant : The addition of sodium perchlorate to the reaction mixture in varying concentrations has without any significant influence on the rate. A decrease in the dielectric constant of the medium (increase in methanol content) increases the reaction rate (Table 3).

TABLE 3—EFFECT OF IONIC STRENGTH AND DIELECTRIC CONSTANT

[CAT]=$5.0\times10^{-4}M$, [As(III)]=$5.0\times10^{-3}M$, [NaOH] =$4.0\times10^{-3}M$, Temp : 0°C

I, M	0.1	0.2	0.4	0.6	0.8	1.0
$k_1\times10^4s^{-1}$	10.53	10.55	10.50	10.60	10.65	10.60
% Methanol (vol/vol) :		Nil	10	20	30	40
$k_1\times10^4s^{-1}$		10.53	11.10	12.50	13.77	14.40

Effect of temperature: Kinetic runs were carried out at 0°, 5° and 10° and the corresponding k_1 values are : 10.53, 14.09 and $20.43\times10^{-4}S^{-1}$ respectively when [AS(III)]=$5.0\times10^{-3}M$; [CAT]=$5.0\times10^{-4}M$ and $[OH^-]=4.0\times10^{-3}M$. Arrhenius equation is found to be applicable in this temperature range which leads to $E_a^{\ddagger}=42.7$ KJ mol^{-1} and $\Delta S^{\ddagger}=-109.3JK^{-1}$ at 273°K. respectively.

Discussion

The ionic strength and dielectric constant effects indicate that the reaction may be between an ion and a dipole. CAT hydrolyses in aqueous solution in accordance with :

$$CH_3.C_6H_4.SO_2NCl.Na + H_2O \rightleftharpoons CH_3.C_6H_4.SO_2NHCl + NaOH$$

$$CH_3.C_6H_4SO_2NHCl + NaOH \rightleftharpoons CH_3C_6H_4SO_2NH_2 + Na^+ + OCl^-$$

The various oxidising species may be CAT itself, *p*-toluene sulphochloramide and OCl^- ion. As the rate is inversely proportional to $[OH^-]$, it is believed that *p*-toluene sulphochloramide is the active oxidising species[10].

Earlier, it has been shown that in alkaline medium arsenic(III), exists as different species viz : $As(OH)_3$, $AsO(OH)_2^-$, $AsO_2(OH)^{2-}$ and AsO_3^{3-} according to the following equilibria :

$$As(OH)_3 + OH^- \rightleftharpoons AsO(OH)_2^- + H_2O \quad ...(1)$$

$$AsO(OH)_2^- + OH^- \rightleftharpoons AsO_2(OH)^{2-} + H_2O \quad ...(2)$$

$$AsO_2(OH)^{2-} + OH^- \rightleftharpoons AsO_3^{3-} + H_2O \quad ...(3)$$

In this connection, it may be mentioned that in the oxidation of arsenic(III) by $Fe(CN)_6^{3-}$ in a highly alkaline medium, Mushran *et al.*[6] observed a first order dependence of rate on OH^-. They have proposed AsO_3^{3-} as the active species of the substrate. The present investigation is carried out in low alkaline conditions ($[OH^-]=4.0-8.0\times10^{-3}M$). Further, the rate is inversely proportional to $[OH^-]$ as in the case of many other reactions of CAT.

In this study, the authors believe that the equilibrium(1) is involved in the concentration range of the $[OH^-]$ employed. Since the inverse dependence of the rate on $[OH^-]$ can be understood from the hydrolysis of CAT, the effect of $[OH^-]$ on equilibrium(1) may be negligible. So it may be assumed that the reaction may be between $CH_3.C_6H_4.SO_2NHCl$ and $AsO(OH)_2^-$ ion. In light of the above observations, the following mechanism is proposed to explain the experimental results.

$$CH_3.C_6H_4.SO_2NClNa + H_2O \underset{k'_{-1}}{\overset{k'_1}{\rightleftharpoons}} CH_3.C_6H_4.SO_2NHCl + NaOH$$

$$CH_3.C_6H_4SO_2NHCl + AsO(OH)_2^- \xrightarrow[slow]{k'_2} CH_3.C_6H_4SO_2NH_2 + AsO_3^- + HCl$$

Applying steady state treatment to the intermediates and with the reasonable assumption that $k'_{-1}[NaOH] >> k'_2[AsO(OH)_2^-]$, the rate law is :

$$-\frac{d[CAT]}{dt} = \frac{k'_1 k'_2 [CAT][AsO(OH)^{-2}]}{k'_{-1}[NaOH]}$$

which is in accordance with the experimental results.

Acknowledgement

GBR and AKR are grateful to the CSIR, New Delhi for the award of junior and senior research fellowships respectively.

References

1. M. M. CAMPBELL and G. JOHNSON, *Chem. Rev.*, 1978, **78**, 65.
2. M. C. AGRAWAL and S. P. MUSHRAN, *J. Phys. Chem.*, 1971, **75**, 838.
3. R. E. DELURY, *J. Phys. Chem.*, 1970, **71**, 54.
4. F. H. WESTHEIMER, *Chem. Rev.*, 1949, **45**, 419.
5. J. G. MASON and A. D. KOWLAK, *Inorg. Chem.*, 1964, **3**, 1248.
6. M. C. AGRAWAL, V. K. JINDAL and S. P. MUSHRAN, *J. Inorg. Nuclear Chem.*, 1970, **32**, 1257.
7. B. B. PAL, D. C. MUKHERJEE and K. K. SENGUPTA, *J. Inorg. Nuclear Chem.*, 1972, **34**, 3433.
8. K. BOTTGER and W. Z. BOTTGER, *Anal. Chem.*, 1927, **70**, 225.
9. A. BERKA, J. VULTERIN and J. ZYKA, "Newer Redox Titrants", Pergamon Press Ltd., London, Ed., 1965, p. 39.
10. E. BISHOP and V. J. JENNINGS, *Talanta*, 1958, **1**, 989.

J. Indian Chem. Soc.,
Vol. LVII, February 1980, pp. 155-159

Dissociation of $PbCl^+$ in Aqueous Solutions and Related Thermodynamic Quantities

A. K. PRASAD and B. PRASAD

Department of Chemistry, Patna University, Patna-800 005

Manuscript received 6 December 1978, revised 30 October 1979, accepted 31 December 1979

The dissociation constant K of $PbCl^+ \rightleftharpoons Pb^{++} + Cl^-$ has been determined from 5° to 40° at 5° intervals from e.m.f. of the cells of the type :

$$Ag \left| AgCl \begin{matrix} HCl & (m_1) \\ PbCl_2 & (m_2) \end{matrix} \right| \begin{matrix} HCl & (m_1) \\ PbCl_2 & (m_2) \end{matrix} \left| \begin{matrix} HCl & (m_1) \\ PbCl_2 & (m_2) \end{matrix} \right. Q.H. \Big| Pt$$

where Q. H. stands for quinhydrone. Assuming B_i in $\log \gamma_i = -\frac{AZ_i^2 \sqrt{\mu}}{1+\sqrt{\mu}} + B_i \mu$ to be additive and independent of ionic atmosphere when $\mu < 0.1$ the thermodynamic dissociation constant K of $PbCl^+$ has been calculated. The value of $\triangle H^\circ$, $\triangle S^\circ$ and $\triangle G^\circ$ have also been calculated.

GARREL and Gucker[1] jointly calculated the dissociation constant of $PbCl^+$ at 25° from the e.m.f. data of Carmody[2] as well as Hannan[3] and found it to be 0.0293 and 0.0289 respectively. Guntelberg[4] from his own e.m.f. measurement found the value of dissociation constant of $PbCl^+$ to be 0.1 at 25°. From the conductance measurement Reighellato and Davies[5] at 18° and Nancollas[6] at 25° found the value of dissociation constant of $PbCl^+$ to be 0.0304 and 0.0255 respectively. The values at 25° differ a lot. It was therefore decided to determine values not only at 25° but also at a number of other temperatures.

A cell of the type :

$$Ag \left| AgCl \begin{matrix} HCl & (m_1) \\ PbCl_2(m_2) \end{matrix} \right| \begin{matrix} HCl & (m_1) \\ PbCl_2(m_2) \end{matrix} \left| \begin{matrix} HCl & (m_1) \\ PbCl_2(m_2) \end{matrix} \right. Q.H. \Big| Pt$$

where Q.H. stands for quinhydrone, was employed for this study. In such a cell hydrolysis of lead chloride as well as formation of $PbOH^+$ and its polymers[7] if any would be negligible on account of the presence of hydrogen ion in significant amount. Since solubilities of quinhydrone and silver chloride in the experimental solution are very small, this is negligible, if any liquid junction potential due to them.

Experimental

A stock solution of hydrochloric acid (G. R. E. Merck) was prepared by diluting the concentrated acid with double distilled water. The strength of stock solution determined volumetrically[8] (Borax method) and gravimetrically[9] (silver chloride method) agreed with each other.

Lead chloride was recrystallised twice with double distilled water containing five drops of hydrochloric acid (G. R. E. Merck). It was then dried carefully at 120°.

The experimental solutions were prepared by delivering the required amount of hydrochloric acid through a calibrated burette into a weighed and dried 500 ml measuring flask. To this solid lead chloride was added. It was then dissolved by adding double distilled water. When it dissolved completely the volume of the solution in the measuring flask was made upto the mark after it attained the room temperature. The measuring flask was weighed again. Buoyancy correction was made and the concentration in molalities of HCl and $PbCl_2$ were calculated. It may be noted that at different temperatures different solutions were prepared.

The experimental solutions were deoxygenated by passing pure nitrogen gas through water, presaturater and then through experimental solution.

Silver-silver chloride electrode was prepared by thermal electrolytic process as recommended by Harned and Ehlers[10]. Analytical grade (Renal, Budapest) quinhydrone was recrystallised and dried following the method of Harned and Wright[11]. The electrode vessel, bridges were similar to those used by Prasad and coworkers[12]. The cells were set up in the same way as done by Sinha and Prasad[13]. Measurements were made with a Tinsley Vernier Potentiometer. Duplicate experiments performed in each case generally agreed within 0.10 mv. In few cases at 35° and 40° differences went upto 0.20 mv. The recorded e.m.f. values are the mean of the duplicate cells. Experimental and other significant data are given in Table 1.

Stoichiometric molalities in mol kg^{-1} are denoted by m_1 in case of HCl and m_2 in case of $PbCl_2$. Due

TABLE 1

Mixture of HCl and $PbCl_2$: $m_1 \times 10^3$	$m_2 \times 10^3$	E in abs. volt	$m_{Pb^{2+}} \times 10^3$	$m_{Cl^-} \times 10^3$	$m_{PbCl^+} \times 10^3$	$\mu \times 10^3$
			Temperature—5°			
2.261	4.515	0.21945	3.572	10.347	0.9441	13.918
2.516	5.013	0.22410	3.874	11.403	1.139	15.277
3.016	6.020	0.23224	4.548	13.584	1.472	18.132
3.520	7.023	0.23900	5.100	15.643	1.923	20.743
4.013	8.010	0.24480	5.673	17.696	2.337	23.368
4.513	9.013	0.24997	6.219	19.745	2.794	25.964
5.008	10.037	0.25460	6.768	21.813	3.269	28.581
			Temperature—10°			
2.260	4.508	0.23190	3.688	10.456	0.865	14.144
2.519	5.017	0.21870	3.985	11.520	1.032	15.505
3.020	6.025	0.22695	4.658	13.703	1.327	18.361
3.522	7.021	0.23385	5.270	15.813	1.751	21.083
4.019	8.025	0.23976	5.834	17.878	2.191	23.712
4.519	9.031	0.24498	6.365	19.915	2.666	26.280
5.013	10.039	0.24964	6.909	21.961	3.130	28.870
			Temperature—15°			
2.269	4.526	0.20802	3.457	10.252	1.069	13.709
2.521	5.026	0.21302	3.733	11.279	1.293	15.013
3.024	6.030	0.22140	4.343	13.398	1.687	17.739
3.532	7.043	0.22846	4.888	15.463	2.155	20.351
4.034	8.043	0.23450	5.410	17.487	2.714	22.896
4.536	9.044	0.23974	5.836	19.416	3.208	25.252
5.040	10.053	0.24454	6.334	21.427	3.719	27.762
			Temperature—20°			
2.269	4.524	0.20260	3.464	10.257	1.060	13.721
2.522	5.029	0.20750	3.752	11.303	1.277	15.055
3.025	6.031	0.21597	4.336	13.392	1.695	17.729
3.529	7.035	0.22303	4.822	15.386	2.213	20.208
4.035	8.045	0.22917	5.286	17.366	2.759	22.654
4.539	9.050	0.23448	5.658	19.247	3.392	24.905
5.042	10.052	0.23932	6.104	21.198	3.948	27.301

Continued...

TABLE 1 (CONTINUED)

Mixture of HCl and $PbCl_2$: $m_1 \times 10^3$	$m_2 \times 10^3$	E in abs. volt.	$m_{Pb^{2+}} \times 10^3$	$m_{Cl^-} \times 10^3$	$m_{PbCl^+} \times 10^3$	$\mu \times 10^3$
			Temperature—25°			
2.259	4.509	0.19697	3.386	10.154	1.123	13.540
2.511	5.012	0.20213	3.756	11.279	1.256	15.035
3.014	6.015	0.21071	4.302	13.331	1.713	17.633
3.510	7.007	0.21794	4.870	15.387	2.237	20.257
4.019	8.022	0.22406	5.197	17.238	2.825	22.434
4.519	9.019	0.22957	5.675	19.213	3.344	24.888
5.020	10.020	0.23441	6.040	21.080	3.980	27.120
			Temperature—30°			
2.260	4.510	0.19237	3.649	10.419	0.861	14.068
2.520	5.017	0.19749	3.966	11.468	1.086	15.399
3.018	6.021	0.20618	4.538	13.577	1.483	18.115
3.519	7.021	0.21340	5.018	15.558	2.003	20.576
4.023	8.031	0.21978	5.543	17.597	2.488	23.140
4.520	9.025	0.22513	5.868	19.413	3.157	25.281
5.006	10.029	0.22996	6.257	21.292	3.772	27.549
			Temperatute—35°			
2.522	5.032	0.19205	3.626	11.180	1.406	14.806
3.024	6.036	0.20097	4.100	13.160	1.936	17.261
3.530	7.044	0.20832	4.622	15.196	2.422	19.816
4.038	8.056	0.21477	5.049	17.143	3.007	22.191
4.541	9.059	0.22040	5.456	19.056	3.603	24.512
5.041	10.056	0.22539	5.825	20.922	4.231	26.748
			Temperature—40°			
2.526	5.039	0.18655	3.241	10.806	1.798	14.047
3.032	6.044	0.19541	3.616	12.692	2.428	16.308
3.538	7.053	0.20304	4.049	14.640	3.005	18.689
4.044	8.055	0.20968	4.499	16.599	3.566	21.096
4.552	9.066	0.21550	4.891	18.509	4.175	23.400
5.059	10.075	0.22055	5.137	20.371	4.938	25.408

to low solubility of $PbCl_2$ μ was confined to 0.03 ionic strength.

Discussion

Leaving out charges on the ions, the e.m.f. of the cells of the type :

$$Ag \left| AgCl \begin{matrix} HCl\ (m_1) \\ PbCl_2(m_2) \end{matrix} \right| \begin{matrix} HCl\ (m_1) \\ PbCl_2(m_2) \end{matrix} \left| \begin{matrix} HCl\ (m_1) \\ PbCl_2(m_2) \end{matrix} Q.H. \right| Pt \qquad (C_1)$$

is given by

$$E = E^\circ + \frac{RT}{F} \ln m_H m_{Cl} \cdot \gamma_H \cdot \gamma_{Cl}$$

Therefore

$$\log m_H \cdot m_{Cl} = \frac{(E - E^\circ)F}{2.30259RT} + \frac{2A\sqrt{\mu}}{1+\sqrt{\mu}} - B\mu \qquad \ldots (1)$$

where $B = (B_H + B_{Cl})$

In equation (1) E° is the standard potential of the cell i.e.

$$E^0_{cell} = E^0_{Q.H.} - E^0_{Ag/AgCl,Cl} \quad \text{(Stockholm Convention)} \qquad \ldots (2)$$

The values of E° of quinhydrone have been used as recommended by Bates[14] (taken from Ives[15] book) and the value of E° of silver–silver chloride at required temperatures are known from the study of Harned and Ehlers[16] as given in Ives' book[17]. The calculated values of E° (abs.volt) of cell at various temperatures are given below :

t°C	5	10	15	20	25	30	35	40
E°	0.48037	0.47939	0.47855	0.47785	0.47730	0.47688	0.47669	0.47658

The values of A on molality scale are taken from the work of Manov, Bates, Hammer and Acree[18]. The value of B in equation (1) as calculated by B. K. Choudhary[19] from the e.m.f of cell (C_2) ;

$$H_2 \mid HCl\ AgCl \mid Ag \qquad (C_2)$$

as reported by Harned and Ehlers[16] are given below :

t°C	5	10	15	20	25	30	35	40
B	0.456	0.444	0.460	0.480	0.490	0.476	0.465	0.467

It has been found from the work of B. Prasad[20] and coworkers that B in activity coefficient equation is additive and independent of the composition of ionic atmosphere at least upto μ=0.07 if the solution continues to be acidic and e.m.f. accuracy is not more than 0.1 mv. So the value of B in cell (C_1) containing a mixture of HCl and $PbCl_2$ will be the same as in cell (C_2) containing pure HCl.

Lead chloride in solution in cell (C_1) is assumed to be dissociated as

$$\begin{matrix} PbCl_2 & \xrightarrow{\text{complete}} & PbCl^+ & + & Cl^- \\ m_2 & & (1-\alpha)m_2 & & m_2 \\ & & \upharpoonleft\!\downharpoonright & & \\ & & Pb^{++} & + & Cl^- \\ & & \alpha m_2 & & \alpha m^2 \end{matrix}$$

$$\begin{matrix} \text{and } HCl & \rightarrow & H^+ & + & Cl^- \\ m_2 & & m_1 & & m_1 \end{matrix}$$

$\therefore\ m_H = m_1 \ \ldots\ (3)\ ; \quad m_{Pb} = \alpha m_2 \ \ldots\ (4)\ ;$

$m_{PbCl} = (1-\alpha)m_2 \ \ldots\ (5)$

$$\text{and } m_{Cl} = m_1 + m_2(1+\alpha) \qquad \ldots (6)$$

$$\therefore\ \mu = m_1 + m_2(1+2\alpha) \qquad \ldots (7)$$

For any particular cell an arbitrary value is assigned to μ. Since A, B and m_H in equation (1) are known hence, m_{Cl} corresponding to this value of μ is found from this equation. As m_1, m_2 are known so with this value of m_{Cl}, α is calculated from equation (6). Now a new value of μ is found from equation (7). The new value of μ is fed in equation (1) and the above process is repeated till μ is constant upto sixth place of decimal. The values of α, m_{PbCl}, m_{Cl}, m_{Pb} corresponding to this μ are taken to be correct.

The dissociation constant K of $PbCl^+$ is given by

$$K = \frac{m_{Pb} \cdot m_{Cl}\ \gamma_{Pb} \cdot \gamma_{Cl}}{m_{PbCl} \cdot \gamma_{PbCl}}$$

$$\text{Applying } \log \gamma_i = -\frac{AZ_i^2\sqrt{\mu}}{1+\sqrt{\mu}} + Bi\mu$$

$$\text{we get } \log \frac{m_{Pb} \cdot m_{Cl}}{m_{PbCl}} - \frac{4A\sqrt{\mu}}{1+\sqrt{\mu}} = \log K - B_1\mu \qquad \ldots (8)$$

$$\text{Where } B_1 = (B_{Pb} + B_{Cl} - B_{PbCl})$$

The plot of L.H.S. of equation (8) against μ gives a straight line. The intercept at μ=0 gave the value of log K and B_1 was obtained from the slope of the line. The plots corresponding to equation (8) at 10°, 25°, 35°, 40° are shown in fig 1. Similar plots are

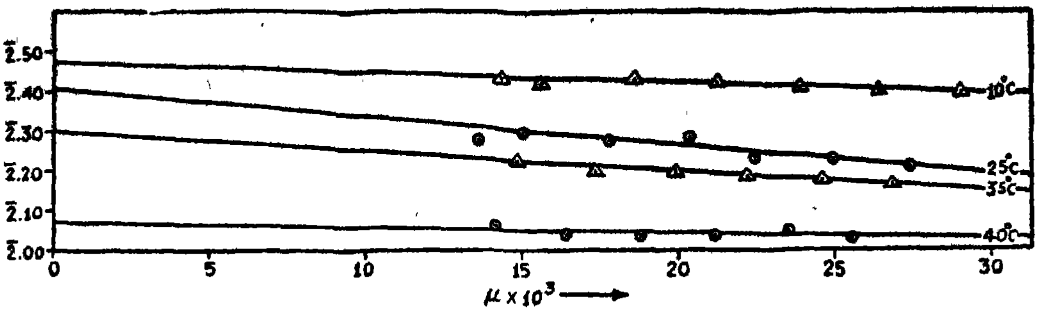


Fig. 1. Equation $\log \frac{m_{Pb} m_{Cl}}{m_{PbCl}} - \frac{4A\sqrt{\mu}}{1+\sqrt{\mu}} = \log K - B_1\mu$

L.H.S.E. plotted against μ

obtained at 5°, 15°, 20° and 30°. The values of K and B_1 are given in Table-2.

TABLE 2

t°C	5	10	15	20	25	30	35	40
B_1	0.916	2.785	2.451	6.575	7.000	12.224	5.100	1.272
$K \times 10^{3}$	2.48	3.01	2.19	2.52	2.57	3.91	2.01	1.18

Lead chloride is bound to be hydrolysed in aqueous solution, due to which some hydrogen ion will be present. This will increase the conductance and so the value of K in case of Nancollas work should have been higher than the present value. But his value is in close agreement of the present value. This is somewhat surprising.

The value of $\triangle H$ has been found from the slope of the straight line obtained by plotting the respective values of log K against $\frac{1}{T}$. The values of $\triangle G°$ at 25° has been found from $\triangle G° = -RT \ln K$ and that of $\triangle S°$ at 25° from $\triangle G° = \triangle H° - T\triangle S°$ (assuming $\triangle H = \triangle H°$).

Reaction	$-\triangle H°$cal/mole
$PbCl^+ = Pb^{++} + Cl^-$	2100 ± 350
$\triangle G°$ cal/mole	$-\triangle S°$cal/degree
2170	14.31

Acknowledgement

The authors are thankful to Bihar State University Commission, Patna and also to the Indian National Science Academy, New Delhi for award of fellowship to one of them (A.K.P.) and to the authorities of the Patna University for library and laboratory facilities.

References

1. R. M. GARREL and F. T. GUCKER (Jr.), *Chem. Rev.*, 1949, 44, 117.
2. W. R. CARMODY, *J. Amer. Chem. Soc.*, 1929, 51, 2905.
3. SISTER M. C. HANNAN, Ph.D. Dissertation. The Catholic University of America, 1936.
4. E. GUNTELBERG, *Chem. Abs.*, 1940, 34, 6507.
5. E. C. REIGHELLATO and C. W. DAVIES, *Trans. Faraday Soc.*, 1930, 26, 592.
6. G. H. NANCOLLAS, *J. Chem. Soc.*, 1955, 1458.
7. D.C. DAS, K. C. SATPATHY and S. PANI, *J. Indian Chem. Soc.*, 1973, 50, 781.
8. A. I. VOGEL, A Text Book of Quantitative Inorganic Analysis, 3rd Edn. E.L.B.S. London, p. 238.
9. A. I. VOGEL, A Text Book of Quantitative Inorganic Analysis, 3rd. Edn., E.L.B.S. London, p. 460.
10. H. S. HARNED and E. H. EHLERS, *J. Amer. Chem. Soc.*, 1929, 51, 416.
11. H. S. HARNED and D. D. WRIGHT, *J. Amer. Chem. Soc.*, 1933, 55, 4849.
12. S. NATH, S. ADITYA and B. PRASAD, *J. Indian Chem. Soc.*, 1951, 28, 683.
13. H. K. SINHA and B. PRASAD, *J. Indian Chem. Soc.*, 1970, 47, 901.
14. R. G. BATES, "Electrometric *p*H Determination", Wiley, New York, 1954, p.175.
15. D. J. G. IVES and G. J. JANZ, "Reference Electrode", Theory and Practice, Academic Press, New York and London, 1961, p. 313.
16. H. S. HARNED and R. W. EHLERS, *J. Amer. Chem. Soc.*, 1933, 55, 2179.
17. D. J. G. IVES and G. J. JANZ, "Reference Electrode", Theory and Practice, Academic Press, New York and London, 1961, p. 189.
18. G. G. MANOV, R. G. BATES, W. J. HAMER and S. F. ACREE, *J. Amer. Chem. Soc.*, 1943, 65, 1765,
19. B. K. CHOUDHARY, Ph.D. Thesis of Patna University, 1972.
20. B. PRASAD, *J. Indian Chem. Soc.*, 1977, 54, 488.

J. Indian Chem. Soc.
Vol. LVII, February 1980, pp. 160-162

Quantitative Treatment of Variation of Specific Conductivity of Sols of Some Colloidal Dyes and Polyelectrolytes with Dilution

B. N. GHOSH

Department of Chemistry, University College of Science,
92, Acharya Prafulla Chandra Road, Calcutta-700 009

Manuscript received 18 September 1979, accepted 9 January 1980

Equations deduced in previous publications to account for the variation of specific conductivity of different types of colloidal electrolytes with dilution (by water) have been subjected to further test using relevant data available in the literature on benzopurpurine 4 B and its isomer prepared from meta-tolidine and also on azrechtic acid, a polyelectrolyte, extracted from the gum of the plant Azadirechta Indica. The equations have been found to hold good in these cases, the concentration and the corresponding specific conductivity varying over a wide range.

IN previous publications[1-4] it has been shown that equations can be deduced from theoretical considerations which account quantitatively for the variation of *p*H and specific conductivity with dilution of a number of colloidal electrolytes. The equation for the variation of specific conductivity λ with dilution is written as follows :

$$\lambda = \theta\lambda_s + (1-\theta)\lambda_i \quad \cdots (1)$$

$$= \theta(\lambda_s - \lambda_i) + \lambda_i \quad \cdots (1a)$$

In the aforesaid equations λ denotes the observed specific conductivity of the sol, containing colloidal material of concentration C (unit arbitrary), θ, the fraction per unit area of an electrode surface (of the conductivity cell) covered by the diffuse electrical double layers of the colloidal particles or macromolecules of the sol and it is equal to $C/(K_0+C)$, K_0 being a constant, λ_s is a proportionality constant and may be interpreted to represent the specific conductivity associated with a unit area of the diffuse double layer at the plane of contact with the electrode surface and λ_i the specific conductivity of the intermicellar solution. λ_i of a highly purified sol must be very small and cannot very much with dilution by distilled water. Its average value may, therefore, be treated as a constant.

Equation (1a) may then be expressed as follows :

$$\lambda = \theta\lambda_a + \lambda_i \quad \ldots (1b)$$

where $\lambda_a = (\lambda_s - \lambda_i)$ and may be treated as a constant specially when λ_s is much greater than λ_i.

However, if λ_i is not very small and varies, even then, equation (1a) may be used in the following form, provided λ_i is determined experimentally ;

$$\lambda_m = \theta(\lambda_s - \lambda_i) \quad \ldots (1c)$$

Where $\lambda_m = (\lambda - \lambda_i)$ and it represents the contribution of the micelles to the specific conductivity of the sol.

Again if some electrolyte is added to the sol so that the specific conductivity of the intermicellar solution becomes relatively high and θ is increased more and more, then correction for the increase of concentration of the electrolyte in the intermicellar solution, caused by the expulsion of the coions and their oppositely charged partner ions from the volume occupied by the colloidal particles and their double layers, has to be introduced. Equation (1) may then be written as follows :

$$\lambda = \theta\lambda_s + \lambda_i(1-\theta)/(1-B\theta^2) \quad .. (2)$$

In equation (2) $\lambda_i/(1-B\theta^2)$ represents the increase of specific conductivity of the intermicellar solution with the increase of θ and λ_i and B are constants. After some simplification, neglecting terms involving θ^3 and higher order terms equation (2) may be expressed as follows :

$$\lambda = \theta(\lambda_s - \lambda_i) + \lambda_i(1+B\theta^2) \quad .. (2a)$$

$$= \theta\lambda_a + \lambda_i(1+B\theta^2) \quad \ldots (2b)$$

The validity of the aforesaid equations has been tested in this paper using the data on benzopurpurine 4B and its isomer prepared from meta-tolidine and on azrechtic acid, a polyelectrolyte.

Variation of specific conductivity of the dye sols with dilution :

Robinson and Mills[5] have investigated at 25° the variation of specific conductivity with dilution (by water) of benzopurpurine 4B and its isomer prepared from

meta-tolidine, after purifying the dyes carefully. For benzopurpurine 4B and its isomer prepared from meta-tolidine, they have used the abbreviations, the "4B dye" and the "meta-dye" respectively and the same abbreviations have been followed in this paper also. The aforesaid authors[5] have observed that 0.5 per cent solutions of the two dyes differ widely in their flocculation values for NaCl. It is also known that the 4B dye is a cotton substantive dye but the meta-dye is not (a cotton substantive dye). In the Tables 1 and 2, λ denotes the specific conductivity of the sol, λ_i the corrected specific conductivity of the ultrafiltrate which is the same as that of the intermicellar solution and $\lambda_m = (\lambda - \lambda_i)$, the specific conductivity contributed by the micelles, C denotes the concentration of the dye in gram equivalents per litre and under the heading miscellaneous are recorded the equation used and the values of the constants K_0 and λ_s.

TABLE 1—VARIATION OF SPECIFIC CONDUCTIVITY OF META-DYE SOLS WITH DILUTION

Miscellaneous	$C\times10^4$	$\lambda\times10^6$	$\lambda_i\times10^6$	Values of $\lambda_m\times10^6$ in recip. ohms. Observed	Calculated
	145.7	1017.4	32.6	984.8	983.0
Equation used -(Ic)	72.85	593.9	21.0	572.9	568.2
	36.43	317.1	13.8	303.3	308.2
	18.22	169.9	9.3	160.6	160.9
$K_0 = 405\times10^{-4}$	4.554	46.39	5.39	41.0	41.6
	1.136	14.61	4.39	10.22	10.46
$\lambda_s = 3748\times10^{-6}$	0.284	6.87	4.26	2.61	2.63

TABLE 2—VARIATION OF SPECIFIC CONDUCTIVITY OF 4B DYE SOLS WITH DILUTION

Miscellaneous	$C\times10^4$	$\lambda\times10^6$	$\lambda_i\times10^6$	Values of $\lambda_m\times10^6$ in recip. ohms. Observed	Calculated
Equation used -(Ic)	133.84	956.5	22.4	934·1	925.4
	66.92	521.5	13.2	508.3	529.6
$K_0 = 405\times10^{-4}$	33.46	293.8	10.15	283.7	285.1
	8.365	85.64	10.85	74.79	75.69
$\lambda_s = 3748\times10^{-6}$	2.092	27.61	7.33	20.28	19.23
	0.5228	12.68	7.72	4.96	4.82

Variation of specific conductivity of azrechtic acid with dilution :

Kulshrestha[6] has investigated the variation of specific conductivity with dilution of sols of azrechtic acid (A R A) in the presence of 0.0005N and 0.002N sulphuric acid at 35°. The (A R A) extracted from the gum of the plant Azadirechta Indica (commonly known as Neem tree) has been purified by electrodialysis before use. His data[6] are recorded in the Tables 3 and 4 in which C denotes the concentration of (A R A) in gram equivalents per liter and λ, λ_a, and λ_i have the same significance as stated already. The values of λ_i found by Kulshrestha[6] at 35° of 0.0005N and 0.002N sulphuric acid solutions in water are 2.41×10^{-4} and 8.8×10^{-4} recip. ohms. respectively.

TABLE 3—VARIATION OF SPECIFIC CONDUCTIVITY WITH CONCENTRATION OF (A R A) IN 0.0005 N H_2SO_4

Miscellaneous	$C\times10^4$	θ	Values of $\lambda\times10^4$ in recip. ohms. Observed	Calculated
Equation used(1b)	2.593	0.0071	2.51	2.50
	10.37	0.0276	2.77	2.77
$K_0 = 3.66\times10^{-3}$	20.74	0.0536	3.09	3.12
	31.10	0.0783	3.42	3.44
$\lambda_a = 13.2\times10^{-4}$	41.50	0.1018	3.74	3.75
	51.87	0.124	4.03	4.05
$\lambda_i = 2.41\times10^{-4}$	62.20	0.145	4.26	4.32
	83.00	0.183	4.86	4.82
	103.70	0.221	5.42	5.33

TABLE 4—VARIATION OF SPECIFIC CONDUCTIVITY WITH CONCENTRATION OF (A R A) IN 0.002 N H_2SO_4

Miscellaneous	$C\times10^4$	θ	Values of $\lambda\times10^4$ in recip. ohms Observed	Calculated
Equation used-(2b)	10.37	0.0276	8.91	8.90
	20.74	0.0536	9.05	9.03
$K_0 = 3.66\times10^{-3}$	31.10	0.0783	9.23	9.20
$\lambda_a = 2.6\times10^{-4}$	41.50	0.1018	9.43	9.39
$\lambda_i = 8.8\times10^{-4}$	51.87	0.124	9.67	9.61
B = 3.6	62.20	0.145	9.77	9.84
	83.00	0.183	10.43	10.34
	103.70	0.221	10.94	10.92

Discussion

It will be noticed from the data recorded in Table 1 that the value of λ_i diminishes as the concentration C of the meta-dye decreases. It is also very small compared to λ_s and its highest value 32.6×10^{-6} is less than 1 per cent of λ_s which is equal to 3748×10^{-6} recip.

ohms. It may also be noted that λ_s remains constant over the entire range of concentration variation of the meta-dye from 14[illegible] $\times 10^{-4}N$ to $0.284 \times 10^{-4}N$. The values of λ_m calculated by using equation (1c) agree well with those observed. It (λ_m) varies with the dilution of the meta-dye sol from 984.8×10^{-6} to 2.61×10^{-6} recip. ohms and its lowest value is appreciably smaller than the specific conductivity, about 3.6×10^{-6} recip. ohms, of the distilled water used for dilution.

The data recorded in Table 2 show that the values of K_0 and λ_s used in equation (1c) for the calculation of λ_m of the 4B dye are the same as those used for the meta-dye. The agreement between the observed and calculated values of λ_m of the 4B dye may be considered satisfactory for all the concentrations except $66.92 \times 10^{-4}N$ and $2.092 \times 10^{-4}N$. It may be that there occured some errata in printing the aforesaid values of C. If it be supposed that the correct values of C are $62.96 \times 10^{-4}N$ and $2.209 \times 10^{-4}N$ instead of $66.92 \times 10^{-4}N$ and $2.092 \times 10^{-4}N$ respectively and calculations are made using these supposedly correct values of C then the calculated values of λ_m are found to be 502.5×10^{-6} and 20.24×10^{-6} which are quite close to the observed values 503.8×10^{-6} and 20.28×10^{-6} recip. ohms.

It may be pointed out that the value of λ_i recorded in Table 3 is the same as that of $0.0005N$ sulphuric acid solution observed by Kulshrostha[6]. It is much smaller than λ_a and hence the term $\lambda_i B\theta^2$ in equation (2b) is small compared to the sum of the other terms and may be neglected without introducing serious error. Equation (2b) then assumes the same form as equation (1b). It will be noticed from the data recorded (in Table 3) that the values of λ calculated by using equation (1b) agree satisfactorily with those observed.

The value of λ_i recorded in Table 4 is the same as that of $0.002N$ sulphuric acid solution but it is much greater than λ_a and hence the term $\lambda_i B\theta^2$ cannot be neglected and so equation (2b) has to be used for the calculation of λ. It will noticed that the values of λ thus calculated agree well with those observed.

References

1. B. N. Ghosh, *J. Indian Chem. Soc.*, 1971, **48**, 185.
2. B. N. Ghosh, *J. Indian Chem. Soc.*, 1972, **49**, 359.
3. B. N. Ghosh, *J. Indian Chem. Soc.*, 1972, **49**, 565.
4. B. N. Ghosh, A. C. S. Symposium Series Colloidal Dispersions and Micellar Behaviour 1975, 9, 316.
5. C. Robinson and H. A. T. Mills, *Proc. Roy. Soc.*, 1931, A131, 576.
6. V. L. Kulshrestha, *J. Polymer. Sci.*, 1962, **58**, 807.

J. Indian Chem. Soc.,
Vol. LVII, February 1980, pp. 163-167

An Attempt to Account Quantitatively the Electro-viscous Effect of Sols of Sodium-Carboxy-methyl Cellulose under Different Conditions

B. N. GHOSH

Department of Chemistry, University College of Science,
92, Acharya Prafulla Chandra Road, Calcutta-700 009

Manuscript received 1 March 1979, accepted 9 January 1980

It has been shown that Smoluchowski equation for electroviscous effect as modified by the author can be used to account quantitatively for the variation of the reduced viscosity, η_{sp}/C, of sodium-carboxy-methyl cellulose (SCMC) sol under such conditions as (1) dilution of the sol with water, (2) alteration of its pH by the addition of an acid or alkali and (3) its dilution with solutions of salts like NaCl, KCl etc., the concentration of the salts being fixed at the desired levels.

It has also been shown that the specific conductivity of the sol is made up of two parts, one part contributed by the macromolecules with their electrical double layers and the other part by the small ions present in the dispersion medium and that the specific conductivity associated with a unit area of the diffuse double layers of the macromolecules does not change appreciably with dilution although the macromolecules undergo slight hydrolysis.

IN previous publications[1-3] it has been shown how Smoluchowski equation for electro-viscous effect of colloids has been modified by the author and the modified equation has been used to account for the viscous properties of a number of colloidal electrolytes and ampholytes quantitavely.

In this paper the application of the modified equation to account for the reduced viscosity, η_{sp}/C of (SCMC) sols under different conditions will be discussed.

Basu and Das Gupta[4] have investigated at 35° the viscous properties of (SCMC) sol under such conditions as (1) its dilution with water, (2) alteration of its pH by the addition of an acid or alkali and (3) its dilution with solutions of salts like NaCl, KCl, etc., the concentrations of the salts being fixed at the desired levels. They[4] have observed that the pH of a 0.04% sol in distilled water is 6.8. Since the pH of (Laboratory) distilled water lies between 6.2 and 6.4, their observation indicates that (SCMC) undergoes slight hydrolysis in water.

The variation of η_{sp}/C with the dilution of (SCMC) by water has been accounted for by using an empirical equation proposed by Fuoss but its variation under other conditions has been explained only qualitatively by the authors[4].

Deduction of the equations :

(1) The Einstein-Smoluchowski equation for electro-viscous effect has been modified by substituting the specific conductivity λ of the sol in place of λ_i the specific conductivity of the dispersion medium and may be written as follows

$$\eta_{sp}/C = K\frac{V}{100}\left[1+\frac{1}{\eta_0 a^2 \lambda}\left(\frac{D\zeta}{2\pi}\right)^2\right] \quad ...(1)$$

It has been shown in previous publications[5-7] that the variation of λ with the concentration C (unit arbitrary) of the colloid in the sol can be represented by the following equation :

$$\lambda = \theta\lambda_s + (1-\theta)\lambda_i \quad ...(2)$$

In equation (1) V is the specific volume of the colloidal material, C the concentration in gram per 100 ml. of the sol, K, a constant equal to 2.5 for spherical particles η_0 and D the viscosity and dielectric constant of the dispersion medium, a the radius and ζ the electro kinetic potential of the particles.

In equation (2) λ_s represents the specific conductivity associated with a unit area of the diffuse double layers (of the particles) at the plane of contact with the surface of an electrode of the conductivity cell and θ the fraction per unit area of the electrode surface in contact with the double layers (of the particles) and it is equal to $C/(K_o+C)$, where K_o is a constant.

Substituting the value of λ in equation (1) and putting $A = \frac{1}{\eta_0 a^2}\left(\frac{D}{2\pi}\right)^2$ it can be written, after simp-

fication, as follows :

$$\eta_{sp}/C \doteq K\frac{V}{100}\left[1+\frac{A\zeta^2(C+K_0)}{\lambda_s(C+K_0\lambda_i/\lambda_s)}\right] \quad ...(3)$$

$$=k_1\frac{m+C}{m_0+C} \quad ...(4)$$

In equation (4), $k_1=K\frac{V}{100}\left(\frac{A\zeta^2+\lambda_s}{\lambda_s}\right)$,

$m=K_0\frac{(A\zeta^2+\lambda_i)}{(A\zeta^2+\lambda_s)}$ and $m_0=K_0\lambda_i/\lambda_s$ and they remain constant when C is varied. When the (SCMC) sol is diluted with water, η_{sp}/C should vary according to equation (4).

(2) When to a sol of (SCMC) at constant concentration an electrolyte such as an acid or alkali is added, ζ in equation (3) diminishes and λ_i increases. λ_s also changes slightly but its change can be neglected compared to that of λ_i. Let us assume that ζ changes to $\zeta[1-a(s-s_0)]$ and λ_i changes to $\lambda_i[1+b(s-s_0)]$ where s_0 represents the initial activity of the H^+ or OH^- ions when no acid or alkali has been added and s the activity of the ion concerned after some acid or alkali has been added. The aforesaid assumption of linear variation of ζ and λ_i with s should hold good so long as the variation of s is not large. Substituting the aforesaid values of ζ and λ_i in equation (3) and taking the ratio of $(\eta_{sp}/C)_s$ and $(\eta_{sp}/C)_0$ and simplifying in the same way as has been done in a previous publication[8] the following relation is obtained

$$R=(\eta_{sp}/C)_s:(\eta_{sp}/C)_0=1-\frac{m(s-s_0)}{m_0+(s-s_0)} \quad ...(5)$$

where $(\eta_{sp}/C)_s$ and $(\eta_{sp}/C)_0$ denote the observed values of the reduced viscosities when the activities of the H^+ or OH^- ions are s and s_0 respectively and m and m_0 are constants.

Equation (5) may be used to account for the variation of the ratio R with the increase of H^+ or OH^- ion activities when an acid or alkali is added to the (SCMC) sol.

(3) When a (SCMC) sol is diluted with a salt solution of sufficiently low but constant concentration its degree of hydrolysis increases as the *p*H of a salt solution[8] in distilled water is considerably lower than 6.8, the *p*H of the (SCMC) sol. Therefore, when the concentration of (SCMC), starting from a very low value, is increased gradually in the presence of a fixed but sufficiently low concentration of a salt like NaCl its degree of hydrolysis decreases and consequently the electric charge of its macromolecules increases since the COONa groups are far more strongly dissociated than the COOH groups. †Under this condition the ζ potential of the macromolecules increases with the concentration of (SCMC) and reaches a limiting value, say ζ_m, determined by the concentration of the added salt. Let us assume that ζ increases with the (SCMC) concentration C, according to the equation $\zeta=\zeta_0\,(1+bc)$, where ζ_0 is the value of ζ when c is nearly zero and b is the coefficient of increment. As c increases ζ increases at first but when the limiting value ζ_m is reached it does not increase any further with c. Substituting $\zeta_0\,(1+bc)$ for ζ in equation (3) and neglecting terms involving c^2 it may be written as follows :

$$\eta_{sp}/C=K\frac{V}{100}\left[1+A\zeta^2(1+2bc)\left\{\frac{C+K_0}{\lambda_s(C+K_0\lambda_i/\lambda_s)}\right\}\right] \quad ...(6)$$

When C is very small compared to K_0 and $K_0\lambda_i/\lambda_s$ in the expression $(C+K_0)/(C+K_0\lambda_i/\lambda_s)$ in equation (6) then it may be neglected and equation (6) after simplification may be written as follows ;

$$\eta_{sp}/C=B+DC \quad ...(6a)$$

Where $B=\left(K\frac{V}{100}\right)(1+A\zeta_0^2/\lambda_i)$ and $D=\left(K\frac{V}{100}\right)$ $(2\,bA\,\zeta_0^2/\lambda_i)$ and they remain constant when C is varied, the range of variation being small.

Again after ζ reaches the limiting value ζ_m further increase of C does not change ζ_m and equation (6) under this condition assumes the same form as equation (4).

Therefore, in the presence of a sufficiently low but fixed concentration of an added salt as C is increased, starting from a very low concentration, η_{sp}/C should increase linearly with C according to equation (6a) until C approaches that value at which ζ becomes nearly equal to ζ_m. After this value of C is reached if it is further increased then η_{sp}/C should diminish according to equation (4).

It is to be noted, however, that as the concentration of the added salt, say NaCl, is increased the ratio of the activities of $Na^+ : H^+$ in the dispersion medium increases and this tends to suppress the degree of hydrolysis of (SCMC) owing to common ion effect and also according to Donnan's theory of membrane equilibrium. Furthermore, it may be noted that the higher the concentration of the added salt in the (SCMC) sol, the lower must be the ζ of the macromolecules in the sol. Therefore, at a sufficiently high salt concentration, rise of ζ as C is increased, starting from a low concentration, should not occur and at the same time the value of ζ should be quite small. Under this condition, λ_i and $K_0\lambda_i$ should have high values and when C is very small compared to $K_0\lambda_i/\lambda_s$ in the denominator in the right hand side of equation (3) then it may be

† Strictly speaking ζ varies inversely as h, the degree of hydrolyses and if h varies inversely as $\sqrt{c}$, then ζ should vary as $\sqrt{c}$, so one may also write $\zeta=\zeta_0\,(1+b\sqrt{c})$

neglected and equation (3) may be written as follows :

$$\eta_{sp}/C = K\frac{V}{100}\left[1+\frac{A\zeta^2(K_0+C)}{K_0\lambda_i}\right]$$
$$= B_1 + D_1C \qquad \ldots(6b)$$

where $B_1 = (kV/100)\ (1+A\zeta^2/\lambda_i)$ and $D_1 = (KV/100)\ (A\zeta^2K_0\lambda_i)$ and they remain constant when C is varied.

It, therefore, follows from equation (6b) that when the concentration of the added salt is fixed at a sufficiently high level, η_{sp}/C should vary linearly with C, the concentration of (SCMC).

(4) In previous publications[5-7] it has been shown that equation (2) holds good for colloids which do not undergo hydrolysis in water. Since (SCMC) undergoes slight hydrolysis in aqueous solution so in this case the validity of equation (2) should be checked.

In equation (2) $\theta = C/(K_0+C)$ and where C is very small compared to K_0 it may be neglected.
Therefore it follows that,

$$\lambda = \left(\frac{C}{K_0+C}\right)\lambda_s + \lambda_i\left(1-\frac{C}{K_0+C}\right)$$
$$= C\lambda'_s, + \lambda_i \qquad \ldots(7)$$

Neglecting $C/(K_0+C)$ compared to unity when C is very small compared to K_0 and $\lambda'_s = (\lambda_s/K_0)$. The data recorded in Table 5 confirm the validity of equation (7) and hence that of equation (2).

Notes on the data recorded in the Tables :

Table 1—(Variation of η_{sp}/C with C in aqueous solution at 35°C

Miscellaneous	(SCMC) per cent C	Variation of η_{sp}/C	
		Observed	Calculated
Eqn. – (4)	0.070	63.5	60.5
$K_1 = 51$	0 053	63.1	63.2
m=0.017	0.040	68.0	67.5
$m_0 = 0.0033$	0.023	76.6	77.6
	0.013	93.2	93.8

Table 2(a)—(Variation of R with increase of (OH^-) activity at 35°C)

Miscellaneous	*p*H	(OH^-) activity S	η_s/η_0	Values of R	
				Observed	Calculated
Eqn. (5)	6.80	1.59×10^{-7}	3.58	1.00	1.00
$s_0 = 1.59\times10^{-7}$	8.80	1.59×10^{-6}	3.44	0.95	0.98
m=0.332	9.50	7.94×10^{-5}	3.39	0.93	0.93
	10.10	3.16×10^{-4}	3.22	0.86	0.83
$m_0 = 2.72\times10^{-4}$	10.54	8.71×10^{-4}	2.93	0.75	0.75

Table 2(b)—(Variation of R with increase of H^+ ion activity at 35°C)

Miscellaneous	*p*H	(H^+) activity S	η_s/η_0	Values of R	
				Observed	Calculated
Eqn. (5)	6.80	1.59×10^{-7}	3.67	1.00	1.00
$s_0 = 1.59\times10^{-7}$	5.80	1.59×10^{-6}	3.35	0.88	0.88
m=0.31	5.50	3.16×10^{-6}	3.28	0.85	0.83
$m_0 = 0.23\times10^{-5}$	4.52	3.02×10^{-5}	2.90	0.71	0.71

Table 3—(Variation of η_{sp}/C with C in NaCl solution at 35°C)

Miscellaneous	(SCMC) per cent C	Values of η_{sp}/C	
		Observed	Calculated
NaCl=0.000214*N*	0.0882	55.6	55.7
	0.0735	58.4	57.4
Eqn. (4)	0.0588	60.9	59.8
$K_1 = 45.8$			
m=0.034	0.0441	64.6	63.5
$m_0 = 0.0123$	0.0294	69.4	69.6
	0.0147	80.7	82.4
NaCl=0.000214*N*	0.0147	80.7	80.6
Eqn. (6a)	0.0072	70.3	71.6
B=63.0	0.0022	65.6	65.6
$D = 1.2\times10^{8}$			
NaCl=0.000521*N*	0 994	45.3	46.0
Eqn. (4)	0.0852	47.6	46.8
$K_1 = 38.4$	0.0710	48.9	48.4
m=0.046	0.0568	51.2	50.1
$m_0 = 0.022$	0.0497	53.92	51.1
	0.0426	53.0	52.7
	0.286	54.2	56.7
NaCl=0.000521*N*	0.0220	—	56.7
Eqn. (6a)	0 0142	51.7	52.1
B=45.0	0.0071	48.8	48.5
$D = 5\times10^{2}$			
NaCl=0.001516*N*	0.0753	30.5	31.5
Eqn. (6b)	0.0568	28.6	28.6
$B_1 = 19.5$	0.0426	27.1	26.3
$D_1 = 160$	0.0355	26.3	25.2
	0.0213	22.9	22.9
	0.0071	20.4	20.6

TABLE 4 – (VARIATION OF η_{sp}/C WITH C IN KCl SOLUTION AT 35°C)

Miscellaneous	(SCMC) per cent C	Value of η_{sp}/C Observed	Calculated
KCl = 0.00041*N*	0.0990	33.1	33.6
Eqn. (4)	0.0880	34.4	34.3
$\kappa_1 = 27.2$			
m = 0.048	0.0770	34.8	35.1
$m_0 = 0.02$	0.0660	36.9	36.1
	0.0550	36.6	37.4
	0.0440	39.9	39.1
	0.0330	42.2	41.6
	0.0220	45.1	45.3
KCl = 0.000416*N*	0.0220	45.1	47.7
Eqn. (6a)			
B = 38.9	0.0110	44.6	43.3
$D = 4 \times 10^{3}$	0.0050	40.9	40.9
KCl = 0.001864*N*			
Eqn. (6b)	0.0768	28.4	28.4
	0.0640	28.2	27.6
$B_1 = 23.5$	0.0517	26.9	26.8
$D_1 = 64.0$	0.0256	26.2	25.1
	0.0128	24.3	24.3

TABLE 5 – (VARIATION OF SPECIFIC CONDUCTIVITY OF (SCMC) WITH DILUTION BY WATER)

Miscellaneous	(SCMC) per cent C	Specific conductivity $\times 10^{-4}$ Observed	Calculated
Eqn. (7)	0.270	9.29	9.16
$\lambda'_s = 33.6 \times 10^{-4}$	0.135	4.529	4.626
$\lambda_i = 9 \times 10^{-4}$	0.068	2.337	2.375
	0.034	1.260	1.233
	0.017	0.653	0.661
	0.008	0.353	0.359

In Table 1 are recorded the data taken from Table 1 of the paper of Basu and Das Gupta[4]. In column 1 of the table under the head 'Miscellaneous', the equation used and the value of each of the constants in the equation have been mentioned.

The data recorded in the Tables 2(a) and 2(b) of this paper have been collected from Table 2 of the paper of the aforesaid authors[4].

The data recorded in the Tables 3,4 and 5 of this paper have been collected from the Tables 3, 4 and 7 respectively of the paper of Basu and Das Gupta[4].

Discussion

It may be noticed from the data recorded in Table 1 that the observed values of η_{sp}/C for different values of C agree well those calculated from equation (4). The observed value of η_{sp}/C at C=0.07 per cent is higher than that at C=0.053 per cent of (SCMC). It is probable that at C=0.07 per cent, the second order electroviscous effect owing to the interaction of the double layers of the macromolecules of (SCMC) is just making itself felt. Equation (4) deals with primary electroviscous effect only and hence the value of η_{sp}/C calculated from it may be a little low.

It is apparant from the data recorded in the Tables 2(a) and 2(b) that the values of R calculated from equation (5) agree well with those observed. It may be pointed out that when the *p*H is diminished by adding HCl to the (SCMC) sol then below *p*H 4.52 equation (5) is no longer applicable as most of the COO-Na groups of SCMC are then converted to the COOH groups.

The data recorded in Table 3 show that at NaCl concentration equal to 0.000214, when the concentration of (SCMC) is varied from 0.088 per cent to 0.0147 per the values of η_{sp}/C calculated from equation (4) agree well with those observed. At or near C=0.0147 per cent η_{sp}/C attains its maximum value. From this value of C, η_{sp}/C decreases linearly as C decreases according to equation (6a). In this region, the ζ potential of the macromolecules decreases, owing to hydrolysis, as C decreases.

At NaCl concentration equal to 0.000521*N* the variation of η_{sp}/C when C is varied from 0.099 per cent to 0.0284 per cent can be quantitatively accounted for by equation (4). It may be noted that η_{sp}/C attains its maximum value between 0.028 and 0.022 per cent of (SCMC) and this maximum value is less than that at NaCl concentration equal to 0.000214*N*.

At NaCl concentration equal to 0.001516*N*. η_{sp}/C varies linearly with C and its values calculated by using equation (6b) agree well with those observed. At this relatively high concentration of NaCl, C in the denominator of the right hand side expression of equation (3) can be neglected compared to $K_0 \lambda_i/\lambda_s$ and equation (3) then assumes the form of equation (6b).

The data recorded in Table 4 show that at KCl concentration equal to 0.000416*N*, variation of η_{sp}/C with C can be quantitatively accounted for by equation (4) when C lies between 0.099 and 0.022 per cent and by equation (6a) when C lies between 0.022 and 0.005 per cent of (SCMC).

At KCl concentration equal to 0.001864*N* η_{sp}/C varies linearly with C according to equation (6b).

The data recorded in Table 5 show that the variation of specific conductivity of the (SCMC) sol with dilution by water can be represented fairly satisfactorily by equation (7). Since equation (7) is only an approximate form of equation (2) so the application of the latter to the (SCMC) system is justified.

References

1. B. N. Ghosh, *J. Indian Chem. Soc.*, 1976, 53, 881.
2. B. N. Ghosh, *J. Indian Chem. Soc.*, 1977, 54, 1086.
3. B. N. Ghosh, *J. Indian Chem. Soc.*, 1978, 55, 254.
4. S. Basu and P. Das Gupta, *J. Colloid. Sci.*, 1952, 7, 53.
5. B. N. Ghosh, *J. Indian Chem. Soc.*, 1972, 49, 359.
6. B. N. Ghosh, *Proc. Indian Nat. Sci. Acad.*, 1972, A30, 45.
7. B. N. Ghosh, A. C. S. Symposium Series, Colloid Dispersions and Micellar Behaviour, 1975, 9, 318.
8. H. S. Harned, *Trans. Faraday Soc.*, 1927, 23, 462.

J. Indian Chem. Soc.,
Vol. LVII, February 1980, pp. 168-171

Anion Exchange Distribution Studies of Some Metal Ions in Aqueous Nitrite and Aqueous Methanol-Nitrite Media

R. P. BHATNAGAR and N. C. JAIN

School of Studies in Chemistry, Jiwaji University, Gwalior, M.P.

Manuscript received 10 October 1979, accepted 30 November 1979

Anion exchange equilibrium distribution of fifteen metal ions have been studied in aqueous nitrite and aqueous methanol nitrite media using Dowex-21K in nitrate form. The ions such as Hg(II), Cd(II) and Ag(I), which were expected to form stable metal nitrite complexes gave high K_D values. Studies in aqueous nitrite media suggested the following selectivity sequence of common transition and post transition ions for the anion exchanger used.

$$Hg(II) > Cd(II) > Ag(I) > Pb(II) > Cu(II) > Zn(II) > Co(II) \approx Ni(II)$$

Out of the less common metal ions studied uranyl (II) and Ce(III) gave quite high distribution values. Separation possibilities for many metal ions by ion exclusion technique have been suggested.

Use of methanol as a water miscible less polar solvent mixed with water increased the K_D values with increasing methanol percentage in the solution generally suggesting stabilization of metal nitrite complexes in such solutions. Utility of such solvents has also been shown for planning certain useful separations.

A variety of complexing media have been used to study the metal ion exchange on anion exchangers and their uses has been done in many analytical separations. Amongst them the mineral acids and their salts form a class of complexing agents which has been used by many workers. Thus the use of hydrochloric acid media has been done by Kraus and Nelson[1] and Bunny *et al.*[2]; while mixed hydrochloric acid-hydrofluoric acid media was used by Nelson *et al*[3]. Pure hydrofluoric acid media was used by Faris (4) to provide elution characteristics of some 50 elements, Kraus and Nelson[1,2,5] have reported metal ion distribution data in pure nitric acid also. Similarly the sulphate[6] and phosphate media have also been used.

As the presence of water miscible polar organic solvents proved advantageous in the metal ion exchange in complexing media. The use of mineral acids and their salts has been done in a variety of non-aqueous and mixed aqueous solvents. Some recent reviews by Korkish[7], Marcus[8] and Strelow[9] summarise their attempts in quite a detailed manner.

A new nitrite media was used by Bhatnagar *et al.*[10] for studying the distribution of some metal ion in aqueous and mixed ethanol media. In this communication anion exchange distribution studies with 15 metal ions using sodium nitrite in aqueous and aqueous methanolic solutions have been reported. The data has been procured on a new commercially available exchanger-Dowex-21K in nitrate form.

Experimental

Exchange Resin :

An anion exchange resin, Dowex-21K in nitrate form was used for all anion exchange distribution studies. It was a strong base anion exchanger of analytical grade (50-100 mesh). The air dried resin (~25°) had a capacity of 3.6 meq./gm. and a moisture contents of ~20%.

Metal ion Solutions

All metal salt solutions were prepared from their nitrates (AR reagents of British Drug House) to give 0.2 *N* stock solutions in aqueous medium. Thus solutions of Ag(I), Tl(I), Pb(II), Cu(II), Zn(II), Cd(II), Co(II), Ni(II), Fe(III), Ce(III) and U(VI) were prepared directly in double distilled water. Minimum quantity of pure nitric acid was added to the stock solutions of Hg(II), (~0.2%) and Zr(IV) (~1%) to check their hydrolysis. Bismuth(III) solution was prepared in presence of mannitol as detailed in an earlier communication[11].

The stock solutions were suitably diluted with double distilled water or with methanol (AR, BDH) and water to give metal ion solution of 0.05 *N* concentration in purely aqueous or aqueous methanolic (20, 40, 60% v/v) solutions.

Determination of Various Elements

Most of these elements as cobalt(II), nickel(II), cadmium(II), zinc(II), lead(II), bismuth(III), zirco

nium(IV) and thorium(IV) were estimated titrimetrically with disodium EDTA using appropriate metal indicator. Silver(I) and mercury(II) were determined with ammonium thiocyanate in nitric acid medium using ferric ion as indicator. Thalium(I) was estimated with potassium iodate. Estimation of copper was done iodometrically. Iron(III) was estimated by permanganate while *Ce(II) was titrated with Mohr's salt* solution. Only uranium(VI) was estimated gravimetrically as oxinate. For metal ion estimation in distribution studies in nitrite media destruction of nitrite ion was a pre-requisite.

Determination of Distribution Coefficient

All distribution studied were performed in glass stoppered Erlenmeyer flasks (250 ml.) with exactly 1 gm. of the resin and 50 ml. of the solution containing the same quantity of metal ion (0.05 N) in aqueous and different methanolic nitrite media. Batches were equilibrated by shaking for 24 hours. Each solution was then analysed for the metal ion.

The weight distribution coefficients (K_D) were calculated from the relation.

$$K_D = \frac{\text{meq metal per 1 gm. of dry resin}}{\text{meq. metal per 1 ml. of solution}}$$

The results have been tabulated in Table 1-4 for aqueous and 20, 40 and 60% (v/v) aqueous methanolic solutions.

TABLE 1—ANION EXCHANGE DISTRIBUTION COEFFICIENTS IN AQUEOUS NITRITE MEDIA ON DOWEX-21K (NO_2^-)

Ions	Nitrite concentrations, N						
	0.1	0.3	0.5	0.7	1.0	1.5	2.0
Ag(I)	7	50	44	19	35	30	42
Tl(I)	0	0	1	2	0	4	4
Hg(II)	ppt	ppt	283	271	173	248	205
Pb(II)	6	17	19	19	19	19	15
Cu(II)	0	2	10	14	26	31	34
Zn(II)	2	4	7	10	17	22	29
Cd(II)	0	27	59	64	89	89	33
Co(II)	1	2	5	10	11	11	18
Ni(II)	3	3	4	2	1	3	5
Fe(III)	6	3	ppt	ppt	ppt	ppt	ppt
Bi(III)	5	23	25	39	—	63	63
Ce(III)	61	122	135	135	167	167	13
UO_2(II)	61	89	61	128	172	ppt	ppt
Zr(IV)	13	6	4	ppt	ppt	ppt	ppt
Th(IV)	44	54	19	18	24	41	44

TABLE 2—ANION EXCHANGE DISTRIBUTION COEFFICIENTS IN 20% (v/v) AQUEOUS METHANOL SOLUTIONS

Ions	Nitrite concentrations, N						
	0.1	0.3	0.5	0.7	1.0	1.5	2.0
Ag(I)	—	—	—	—	—	—	—
Tl(I)	1	6	11	26	8	27	106
Hg(II)	ppt	ppt	251	172	169	271	205
Pb(II)	12	28	32	32	28	23	21
Cu(II)	5	26	28	39	70	84	58
Zn(II)	3	10	12	19	25	28	38
Cd(II)	14	75	78	89	38	19	38
Co(II)	1	5	8	37	40	44	59
Ni(II)	3	5	6	1	5	5	14
Fe(III)	2	ppt	ppt	ppt	ppt	ppt	ppt
Bi(III)	—	—	—	—	—	—	—
Ce(III)	167	166	134	234	396	ppt	ppt
UO_2(II)	137	102	108	54	ppt	ppt	ppt
Zr(IV)	19	142	ppt	ppt	ppt	ppt	ppt
Th(IV)	24	25	13	13	27	93	111

TABLE 3—ANION EXCHANGE DISTRIBUTION COEFFICIENTS IN 40% (v/v) AQUEOUS METHANOL SOLUTIONS

Ions	Nitrate concentrations, N						
	0.1	0.3	0.5	0.7	1.0	1.5	2.0
Ag(I)	—	—	—	—	—	—	—
Tl(I)	0	6	0	0	2	3	5
Hg(II)	ppt	ppt	163	117	162	205	140
Pb(II)	24	32	32	32	25	19	16
Cu(II)	ppt	ppt	ppt	55	131	133	92
Zn(II)	5	19	27	38	38	48	52
Cd(II)	5	65	105	7	122	24	15
Co(II)	6	11	26	26	37	37	82
Ni(II)	5	8	3	5	6	14	27
Fe(III)	3	ppt	ppt	ppt	ppt	ppt	ppt
Bi(III)	—	—	—	—	—	—	—
Ce(III)	62	102	ppt	ppt	ppt	ppt	ppt
UO_2(II)	55	36	23	32	ppt	ppt	ppt
Zr(IV)	33	1	ppt	ppt	ppt	ppt	ppt
Th(IV)	23	10	6	12	8	23	23

TABLE 4—ANION EXCHANGE DISTRIBUTION COEFFICIENTS IN 60% (v/v) AQUEOUS METHANOL SOLUTIONS

Ions	Nitrite concentrations, N						
	0.1	0.3	0.5	0.7	1.0	1.5	2.0
Ag(I)	*—	—	—	—	—	—	—
Tl(I)	0	0	0	0	0	3	3
Hg(II)	ppt	ppt	137	169	140	162	119
Pb(II)	38	56	54	46	39	32	27
Cu(II)	ppt	ppt	ppt	ppt	235	254	95
Zn(II)	4	21	38	44	44	52	52
Cd(II)	6	111	97	46	27	20	65
Co(II)	6	41	59	66	47	47	47
Ni(II)	8	9	17	21	31	41	52
Fe(III)	3	ppt	ppt	ppt	ppt	ppt	ppt
Bi(III)	—	—	—	—	—	—	—
Ce(III)	ppt	ppt	ppt	ppt	ppt	ppt	ppt
UO_2(II)	73	60	28	44	ppt	ppt	ppt
Zr(IV)	158	ppt	ppt	ppt	ppt	ppt	ppt
Th(IV)	12	2	0	0	0	9	27

During the preparation of the solution phase insoluble compounds were formed in some cases. Such cases have been indicated by ppt in the tables. No distribution studies could be done in such cases.

Results and Discussion

The study of usual type of ion-exchange equilibria is useful in predicting the selectivity trends for ions of different types under the experimental conditions. But when a complexing agent is present in the solution phase, the exchange equilibria is modified according to the nature of the complexed species in the solution. Thus in such cases two equilibria are at work in the solution phase – (1) ion exchange equilibria and (2) the complex equilibria. The nature of the complexed ion formed due to the complex equilibria decides the fate of the sorbable ion on an exchanger.

If the complexing ligand is a negative ion, it may lead to stepwise formation of complexes of various types differing in the overall change of the species. Nitrite ion is such an ion which can form several ionic species in solution with metal ions, finally giving stable negatively charged complexed ions. If such a system is brought in contact with an anion exchanger, we can expect more and more metal ion uptake (as a negatively charged complexed ion) with increasing concentration of the negatively charged ligand. This is so when the metal-nitrite complex is a stable negatively charged species. Formation of less stable complexes or no complex formation at all may lead to lesser or no exchange on an anion exchanger. Hence measured K_D values may be regarded as a rough measure of the stabilities of the complexes.

The results of Table I can now be considered to see the effect of the added sodium nitrite to the metal ion uptake by an anion exchanger. Practically in all the cases the metal ion distribution coefficients have shown an increase upto a certain nitrite concentration. But the maximum K_D values were obtained at different nitrite concentration in different cases.

Mercury(II) gave maximum K_D at 0.5 N nitrite concentration, while silver(I) could give it between 0.3 – 0.5 N. Cadnium(II) gave a maximum at 1.0 – 1.5 N nitrite concentration. Similarly both Ce(III) and uranyl ions gave maximum K_D values at ~1.0 N nitrite concentration. All these ions have been considered to be forming quite stable nitrite complexes. Very high values of K_D for Hg(II) are indicative of this fact. Though these values decreased a bit by increasing nitrite concentration from 0.5 to 0.7, 1.0 or 1.5 M, but still they were highest of all ions studied. Thus Hg(II) nitrite complexes were the most preferred complexed species for Dowex-21K.

Out of the other common transition and post transition metal ions Cd(II) and Ag(I) were much preferred by this resin as compared to ions as Co(II), Ni(II), Cu(II) and Pb(II). From the K_D data of metal ions in Table I can be given the following selectivity sequence for the anion exchanger studied.

$$Hg(II) > Cd(II) > Ag(I) > Pb(II) > Co(II)$$

$$Zn(II) > Co(II) \approx Ni(II)$$

The higher K_D value of 62 for Bi(III) which does not give nitrite complex can be due to considerable electrolytic sorption in presence of this salt (or may it be mannitol). Similarly zero or negligibly small values of K_D for Tl(I) are also due to the fact that it does not form nitrite complexes[11,12].

It is thus clear from Table 1 that Hg(II) can be separated from Tl(I), Pb(II) and Bi(III) at any nitrite concentration above 0.5 N. Very good ion exclusion separations can be carried out for these later metal ions from Hg(II) in nitrite media. Results also show possibilities of Cd(II) separations from Cu(II), Zn(II), Ni(II) and Co(II) at about 1.0 N nitrite concentration.

Amongst the less familiar ions such as UO_2(II), Ce(III), Th(IV) and Zr(IV) the separation of Ce(III) from Th and Zr can be planned at about 0.5 N nitrite concentration. Uranyl ion can be conveniently separated from Th(IV) at any nitrite concentration from 0.7 – 1.0 N. The anion exchange sequence for these ions in nitrite media may be written as :

$$Ce(III) > UO_2(II) > Th(IV) > Zr(IV)$$

Considering now the results of metal ion distribution in aqueous methanolic solutions (Table 2 to 4) it can be said that generally for transition metal ions the distribution of the metal ion on an anion exchanger increased with increasing methanol concentration. It was true for all these cases where no precipitation was seen in mixed solvent systems. But for Hg(II) the trend was opposite.

It has been shown by several authors[10-17] that the presence of a less polar solvent mixed with water, enhances the extent of complex formation. This is why the distribution coefficients of Pb(II), Cu(II), Co(II), Ni(II), Cd(II) showed an increase in solvents with higher methanol concentration. The peculiar trend in Hg(II) might be due to increased ion pair formation in solvents of lower dielectric constants (i.e. with 40 or 60% methanol).

The use of water miscible organic solvents thus definitely modifies distribution tendencies of different ions on an anion exchanger. Hence such systems can provide better K_D values for certain pairs of ions to get separated. Thus separation of Cd(II) from Zn(II) Ni(II) can be anticipated in 60% methanol at 0.3 N nitrite concentration. At a higher nitrite concentration (1.5N)Cu(II) – Cd(II) separation possibilities can also be predicted. Of course the use of such mixed solvents did not prove useful for ions such as Ag(I), Bi(III), Fe(III), Zr(IV), Ce(III), UO_2(II) etc. as they gave precipitation on adding nitrite to mixed solvents apparently due to insolubility of electrolytes used.

References

1. K. A. Kraus and F. Nelson, *Proc. Intern. Conf. Peaceful Uses Atomic Energy, Geneva*, 1956, 7, 113.
2. L. R. Bunny, N. E. Ballon, N. Pasckal and S. Foli, *Anal. Chem.*, 1959, 31, 324.
3. F. Nelson and K. A. Kraus, *J. Amer. Chem. Soc.*, 1964, 76, 5916.
4. J. P. Faris, *Anal. Chem.*, 1960, 32, 520.
5. K. A. Kraus and F. Nelson, ASTM. Spec. Tech. Publ., 1958, 195, 27.
6. E. S. Freilling, J. Pasckal and A. A. Delvechi, *Anal. Chem.*, 1959, 31, 330.
7. J. Korkish, in "Progr. Nuclear Energy", Pergamon Press, Oxford, Series IX, 1966, Vol. 6, p. 1.
8. Y. Marcus, in "Ion Exchange and Solvent Extraction, Marcel Dekker, Inc. New York, 1973, Vol. 4, 1.
9. F. W. E. Strelow, in "Ion Exchange and Solvent Extraction", Marcel Dekkar, Inc. New York, 1973, Vol. 5, 122.
10. R. P. Bhatnagar, R. G. Trivedi and Y. Bala, *Talanta*, 1970, 17, 249.
11. R. P. Bhatnagar and R. G. Trivedi, *Indian J. Chem.*, 1967, 5, 166.
12. R. P. Bhatnagar and R. G. Trivedi, *J. Indian Chem. Soc.*, 1965, 42, 53.
13. R. W. Gable and N. P. Strobel, *J. Phys. Chem.*, 1965, 60, 513.
14. J. S. Fritz and D. J. Pietrzyk, *Talanta*, 1961, 8, 143.
15. J. S. Fritz and T. A. Rittiz, *Anal. Chem.*, 1962, 34, 1517.
16. D. J. Pietrzyk and D. L. Kizser, *Anal. Chem.*, 1965, 37, 233.
17. D. J. Pietrzyk and D. L. Kizser, *Anal. Chem.*, 1965, 37, 1978.

J. Indian Chem. Soc.,
Vol. LVII, February 1980, pp. 172-174

Studies on the Transformation of Iron Phosphates in Buffer and Acid Soil Systems

A. HAJRA and S. N. CHAKRAVARTI

Vivekananda College, Calcutta and Barasat Govt. College, Barasat, 24-Parganas

Manuscript received 22 February 1977, accepted 9 January 1980

Chemical transformation of different iron phosphates in contact with buffer and acid soils systems at different pHs 4.8, 5.2, 5.8 and 6.2 were studied. The results indicate that these iron phosphates undergo hydrolysis reactions and basic (hydroxy) phosphates were ultimately converted to $FePO_4.2H_2O$. Such transformation were effected by different probable chemical reactions.

HSU and Jackson[5] observed that the transformation of iron phosphates in soils were mainly controlled by *p*H. Bache[1] determined solubility. Products for strengite ($FePO_4.2H_2O$) in pure systems and stated that strengite is never likely to be in equilibrium with any soil solution. He concluded that surface reactions are likely to be responsible for the few reports of ion activity products in soils which are of the same order as that of strengite. This may explain the observation of Chakravarti and Talibudeen[2] who concluded that compounds approximately to the composition of strengite may occur in the temperate climate soils in the *p*H range 3.8 to 4.2.

Larson[6] pointed out that co-existence of various iron, aluminium and calcium in the form of surface complex in soils is particularly likely since *p*H of a given soil may show considerable local variations.

The favourable and unfavourable effects of iron phosphates as fertilizers observed by McGeorge and Breazeale[7] and Dalton *et al.*[8] respectively were probably associated with chemical transformation of iron phosphates in soils.

The studies of changes of composition of iron phosphates in contact with buffer and acid soils are limited, although from phosphate fertility status determination of acid soils, these studies are important.

Experimental

Two ferric phosphates were used: (1) Purchased Fe-P, designated as Fe-P (A) from Albright and Wilson Ltd., London: Analysis gave $Fe_2O_3/P_2O_5=1:1$ corresponds to $FePO_4$ (2) prepared Fe-P, designated as Fe-P (B), was prepared as follows:

Ferric hydroxide was prepared from ferric chlorides washed salt free and suspended in water. Ammonium phosphates was then added and the suspension adjusted to *p*H 2.5 by the addition of phosphoric acids. The resultant product was washed with water, till phosphate free and then washed with alcohol and benzene and finally dried in air at 40°. The orange brown product was lightly ground in agate mortor before use. Analysis gave $Fe_2O_3 : P_2O_5 : 1:2.5$. It is a mixture of $Fe(OH)(H_4PO_4)$ and $Fe(H_2PO_4)_3$ (Gasser & Bloomfield[4]).

In order to study the transformation of iron phosphates at different *p*Hs in buffer solutions, 0.5g samples of the two iron phosphates (Fe-P(A) & Fe-P(B)) were taken in cellophane bags with 5 ml distilled water and a few drops toluene and the bags were kept suspended by threads in 200 ml phthalate-NaOH buffer mixtures[9] at *p*Hs 4.8, 5.2, 5.8 and 6.2 for 6 months. The buffer mixtures also contained a few drops of toluene and the systems were subjected to occasional shaking. After the period chemical analyses were performed to determine the change in composition in the original phosphate. Iron was determined by dichromate after reduction with $SnCl_2$ and phosphate by ammonium molybdate precipitation followed by dissolution in NaOH and back titration with standard acid[10].

In order to study the transformation of different iron phosphates at different *p*Hs in contact with soil water suspension 20 gms samples of soils K, J, T and M (*p*H 4.8, 5.2, 5.8 and 6.15 respectively) were taken with 200 ml water and a few drops of toluene in stoppered bottles and 0.5 g of samples of the bottles and 0.5g of samples of the phosphates in cellophane bags with 5 ml distilled water and a few drops toluene were then allowed to come in contact with the soil-water mixtures. The mixtures were then left for 6 months for equilibrium with occasional shaking. After the period, changes in composition in the original phosphates were determined by chemical analyses as before.

The characteristics of the acid soils are tabulated in Table 1 and the changes in composition of the iron phosphate samples as shown by the ratio $Fe_2O_3 : P_2O_5$ undergone in contact with buffer and soil water suspensions are given in Tables 2 and 3 represented graphically in Fig. 1.

TABLE 1 — SOME CHARACTERISTICS OF ACID SOILS

Locality	Latitude and Longitude of the place	Family	CO_2 effervescence with HCl	pH	Organic carbon %	C.E.C me/100 gms	% of HCl soluble Fe_2O_3	Al_2O_3	P_2O_5
1. Kaksa (K). Burdwan West Bengal	23°28′ N+ 87°26′ E	Lateritic	nil	4.80	0.43	5.25	4.45	5.05	.084
2. Jalpaiguri (J) West Bengal	26°30′ N+ 88°45′ E	Forest Dooars region	,,	5.20	1.55	2.14	2.75	3.64	0.21
3. Thimpoo (T) Bhutan	27°30′ N+ 89°30′ E	Hilly Forest	,,	5.80	1.72	11.45	3.80	4.65	0.13
4. Mohammed Bazar (M) Birbhum West Bengal	24°2′ N+ 87°2′	Lateritic	,,	6.15	0.52	10.35	3.05	4.35	0.076

TABLE 2—CHANGE IN COMPOSITION OF IRON PHOSPHATE FE-P (A) IN

(a) Buffer systems

Buffer pH	Fe_2O_3 mole %	P_2O_5 mole %	Fe_2O_3 P_2O_5	*Probable reactions*
1. Untreated Fe-P(A)	0.18	0 18	1.00	$Fe_2O_3+P_2O_5+4H_2O \rightarrow 2FePO_4.2H_2O$ [or $2Fe(OH)_3.H_3PO_4$]
2. 4.8	0.19	0.17	1.10	unchanged (—do—)
3. 5.2	0.22	0.18	1.20	unchanged (—do—)
4. 5.8	0.23	0.15	1.53	$3Fe_2O_3+2P_2O_5+10H_2O \rightarrow (H_2PO_4)_2$ $Fe\text{-}O\text{-}Fe(H_2PO_4)_2+4Fe(OH)_3 4FeO.OH+4H_2O$
5. 6.2	0.24	0.16	1.50	—do—

(b) Soil Systems

Soil	pH	Fe_2O_3 mole %	P_2O_5 mole %	Fe_2O_3 P_2O_5	*Probable reactions*
1. K	4.8	0.18	0.18	1.00	Same as in (2) in Table 2 (a)
2. J	5.2	0.22	0.17	1.29	Same as in (3) in Table 2 (a)
3. T	5.8	0.24	0.16	1.50	Same as in (4) in Table 2 (a)
4. M	6.15(≃6.2)	0.24	0.16	1.50	Same as in (5) in Table 2 (a)

TABLE 3—CHANGE IN COMPOSITION OF IRON PHOSPHATE FE-P (B) IN

(a) Buffer systems

Buffer pH	Fe_2O_3 mole %	P_2O_5 mole %	Fe_2O_3 P_2O_5	*Probable reactions*
1. Untreated	0.12	0.30	0.40	$2Fe_2O_3+5P_2O_5+11H_2O \rightarrow 2Fe(OH)(H_2PO_4)_2 + 2Fe(H_2PO_4)_3$
2. 4.8	0.18	0.50	0.36	$Fe_2O_3+3P_2O_5+6H_2O \rightarrow 2Fe(H_2PO_4)_3$
3. 5.2	0.20	0.40	0.50	$Fe_2O_3+2P_2O_5+4H_2O \rightarrow (H_2PO_4)_2\text{-}O\text{-}Fe(H_2PO_4)_2$
4. 5.8	0.21	0.28	0.75	(i) $2Fe_2O_3+2P_2O_5+7H_2O \rightarrow (H_2PO_4)_2 Fe\text{-}O\text{-}Fe(H_2PO_4)_2+3Fe(OH)_3 \rightarrow 3FeO.OH+3H_2O$ or (ii) $Fe_2O_3+P_2O_5+4H_2O \rightarrow 2FePO_4.2H_2O$ [or $2Fe(OH)_3.H_3PO_4$]
5. 6.2	0.23	0.27	0.65	—do—

(b) Soil systems

Soil	pH	Fe_2O_3 mole %	P_2O_5 mole %	Fe_2O_3 P_2O_5	*Probable reations*
1. K	4.8	0.20	0.67	0.34	Same as in (2) in Table 3 (a)
2. J	5.2	0.22	0.43	0.51	Same as in (3) in Table 3 (a)
3. T	5.8	0.23	0.27	0.85	Same as in (4) in Table 3 (a)
4. M	6.5	(≃6.2) 0.24	0.24	1.00	Same as in (5) in Table 3 (a)

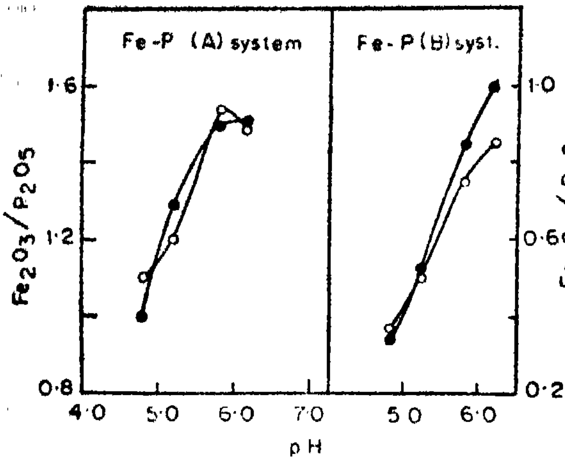


Fig. 1. Change in composition of Fe–P systems in buffer and soil systems.
O—Buffer system
●—Soil system

Results and Discussion

It can be observed from the tables that in case of the hydrated ferric phosphate purchased the Fe_2O_3/P_2O_5 ratios increased from 1.1 to 1.53 and for the prepared basic ferric phosphate the values changed from 0.36 to 0.85 in buffer systems at different *p*H. The probable chemical reactions occurring in such changes are given in the respective tables. Table 3 also indicate a more or less similar rise with such iron phosphates in Fe_2O_3/P_2O_5 ratio with K, J, T & M soils as in case of buffer systems.

In case of soils, however, in general sharper changes in Fe_2O_3/P_2O_5 ratios than in buffer system were observed. These changes are probably influenced by the content of soluble phosphates aluminium, iron etc., present in such soils. The results indicate that basic (hydroxy) phosphates are more susceptable to chemical change than the more stable $FePO_4.2H_2O$ or $Fe(OH)_2.H_2PO_4$. Basic phosphates ultimately converted to $FePO_4.2H_2O$.

The changes in chemical composition probably associated with hydrolysis reactions, and exchange reactions of acid radical H_2PO_4 ion for OH groups; followed by condensation process leading to products of continuously increasing complexity and removal of H_3PO_4 molecules from cellophane bags. Such process can be considered by assuming the properties of H_2PO_4' to be similar to ClO_4' or NO_3' as all these are weak ligands in the *p*H 5-0 to 7-0 and susceptible to ionization at least partly as in case of $Fe(ClO_4)_3$ or $Fe(NO_3)_3$ (Remy[8]).

The following reactions may occur :

(a) $3FePO_4+6H_2O \rightarrow Fe(H_2PO_4)_3+2Fe(OH)_3 \rightarrow 2FeO.OH+2H_2O$

(b) $Fe(H_2PO_4)_3+2H_2O \rightarrow Fe(OH)_2+H_3PO_4$

(c) $2FePO_4+5H_2O \rightarrow Fe(OH)_2H_2PO_4+Fe(OH)_3 +H_3PO_4$

(d) $FePO_4+H_2PO_4'(\text{from soil}) \rightarrow (Fe(PO_4)_2)^{-3}+2H^+$

(e) $FePO_4+2H_2O \rightarrow FeO.OH+H_3PO_4$

(f) $2Fe(H_2PO_4)_3+H_2O \rightarrow (H_2PO_4)_2\ Fe\text{-}O\text{-}Fe\ (H_2PO_4)_2+2H_3PO_4$

(g) $2(H_2PO_4)_2\text{-}Fe\text{-}O\text{-}Fe(H_2PO_4)_2+H_2O \rightarrow (H_2PO_4)_2\text{-}Fe\text{-}O\text{-}\underset{H_2PO_4}{Fe}\text{-}O\text{-}\underset{H_2PO_4}{Fe}\text{-}O\text{-}Fe\ (H_2PO_4)_2 + 2H_3PO_4$

Hydrolysis products of this kind can exist in eqilibrium with the normal salts (or its ions) even in relatively strongly acidic condition. With decreasing H^+ ion concentration, the equilibria may undergo a continuous displacement in the direction of further increase in the particle size i.e. colloidal dispersion until these particles undergo conversion into pure iron hydroxide FeO.OH, by elimination of the last acidic groups. Ultimately, however, unless the solutions are strongly acidic iron hydroxides may be deposited as the stable and product of hydrolysis in the form of FeO.OH, goethite, However, such hydrolysis equilibria can be reached only very slowly hydrolysis equilibria after in course of month.

Acknowledgement

The authors after their sincere thanks to Dr. B. B. Roy, Dean and Acharya P. C. Ray Professor of Agricultural Chemistry, Calcutta University for providing the laboratory facilities and to Dr. N.C. Chattopadhyay, Department of Agriculture, Calcutta University for his kind interest.

References

1. B. W. BACHE, *J. Soil. Sci.*, 1963, 14, 113-123.
2. S. N. CHAKRAVARTI and O. TALIBUDEEN, *J. Soil. Sci.*, 1962, 13, 231-240.
3. J. D. DALTON, G. C. RUSSEL and D. H. SIELING, *Soil. Sci.*, 1952, 73, 173-181.
4. J. K. R. GASSER and C. BLOOMFIELD, *J. Soil. Sci.*, 1955, 6, 219-232.
5. P. H. HSU and M. L. JACKSON, *Soil. Sci.*, 1960, 90, 16-24.
6. S. LARSON, Advances in Agronomy, 1962, 19, 151-210, A. G. Norman, ed.
7. W. T. MCGEORGE and J. F. BREAZEALE, *Arizona Agri. Expt. Sta Tech. Bull.*, 1932, 40.
8. H. REMY, Treatise on Inorganic Chemistry : Translated by J. S. Anderson in English 1956, Vol. 2 ; Elsevier Publishing Company 1956, p. 272-274.
9. A. I. VOGEL, A text book of Macro and Micro qualitative Inorganic Analysis, Longmans Green & Co. Inc. 1959, p. 645.
10. A. I. VOGEL, A text book of Quantitative Inorganic Analysis, ELBS Publication, 1961.

J. Indian Chem. Soc.,
Vol. LVII, February 1980, pp. 175-179

Studies on the Effect of Phosphate, EDTA and Added Micronutrient on the Availability of Zinc in Soil

ASIT KUMAR PAL and BISWANATH DAS

Department of Agril. Chemistry and Soil Science, Bidhan Chandra Krishi Viswa Vidyalaya, Kalyani, West Bengal

Manuscript received 22 August 1979, accepted 9 January 1980

The DTPA-extractable zinc status of two alluvial soils on incubation at moisture saturation under native and fertilized conditions have been studied. It was found that the application of a lower dose of phosphate caused an immediate increase in available Zn in both native and Zn treated soils but with higher dose of phosphate and on prolonged incubation a general decrease was observed. On adding organic matter as EDTA, phosphate treated soils showed an increase but one of the Zn-treated soils showed a decreasing trend which is the general case for all soils on prolonged incubation.

MICRONUTRIENT elements in plant nutrition are of great consequence in agricultural practices. Most of the arable soils are generally well supplied with micronutrients but their availability to plants being dependent on various factors and general plant requirement for these elements being low both deficiency and toxicity effects of them are often encountered. In recent years, the interest in micronutrients has increased because of the increasing consumption of fertilizers, intensive cropping and use of high yielding varieties.

As the ultimate source of micronutrients is the soil, it is necessary to know the available micronutrient status of the soil and the effect of various treatments on the change of availability of such micronutrients. Among the various methods, the DTPA-extraction developed by Lindsay and Norvell[1] has been found to be best correlated with the plant uptake.

Mandal and Das[2] carried out moisture incubation studies on the changes in DTPA-extractable Fe, Mn and Cu status of a few alluvial soils. The present investigation has been undertaken to study the effects of phosphatic and zinc fertilizers with or without an added chelating organic reagent like EDTA on the changes in DTPA-extractable zinc level in two soils of West Bengal on incubation for different periods at moisture saturated condition.

Experimental

Soils: Two soils used in the present investigation were obtained from a farm at Kalyani (K-soil) and from a village of Burdwan (B-soil) respectively. The fields from which the upper 23-cm layer of the soils were collected are under the programme of intensive cultivation. Both the soils are light to medium-textured and belong to recent Gangetic alluvium which have no sharp profile development. The soils were air-dried, ground and sieved through 80-mesh sieve and analysed for various physico-chemical properties which are reported in Table 1.

TABLE 1—PHYSICO-CHEMICAL CHARACTERISTICS OF THE SOILS

Mechanical composition	Kalyani soil	Burdwan soil
Sand %	57.50	47.35
Silt %	5.00	6.00
Clay %	37.50	44.00
*p*H	7.80	6.70
Total Nitrogen %	0.12	0.10
Organic carbon %	0.76	0.75
CEC, me/100 g	9.96	14.70
Saturation percentage	45.20	39.06
Available phosphorus (ppm)	2.75	1.50
Available manganese (ppm)	15.10	35.10
Available zinc (ppm)	1.60	1.20

Treatments and procedure: Each soil was mixed with a basal dose of nitrogen as $(NH_4)_2SO_4$ and potassium as KCl (N=75 ppm, K_2O = 50 ppm) and divided into two main parts. One part was kept as control while the other part was treated with one or more of the following substances: 50 ppm P_2O_5 as single superphosphate (P_1), 100 ppm P_2O_5(P_2), 2 gm EDTA per kg of soil (OM_1) and 20 ppm Zn as $ZnSO_4 \cdot 7H_2O$ (Zn_1).

After thorough mixing, 1 kg of each soil sample were taken in plastic pots. Each of these treated and control samples had three replications. These were

moisture saturated by adding de-ionized water and subjected to incubation for different periods of time such as 1 day, 7 days and 30 days. No holes were left at the bottom of the pots to prevent leaching of the nutrients and the pots were covered with polythene sheets to prevent any loss of moisture.

Weighed portions (about 10 gm) of soil were sampled out with a spoon-headed spatula after each incubation period for extraction of zinc with DTPA extractant.

Extraction : The soil (10.0 gm) was shaken with 20 ml of the DTPA-extractant solution for 2 hours and filtered. To the filtrate 3 ml of conc. nitric acid and 5 ml of conc. sulphuric acid were added and the resulting solution was digested on a hot plate. Another 2 ml of conc. HNO_3 were added until all the organic matter and the metal-DTPA chelates completely decomposed. The resulting material was taken with redistilled water and the volume was made upto mark in 50-ml volumetric flask. Appropriate aliquots were taken from this solution for the estimation of zinc by standard colorimetric methods.

Estimation of zinc : DTPA-extractable zinc was determined by Atomic Absorption Spectrophotometer using acetylene-air flame and a zinc hollow cathode.

Total zinc was estimated colorimetrically by dithizone mthod following the procedure as described by Black[8].

A Klett-Summerson double beam colorimeter was used for all color absorbance measurements.

All the chemicals and reagents used were of A. R. quality.

Results and Discussion

The effect of addition of two different doses of phosphate on the quantity of DTPA-extractable zinc in native and the micronutrient treated soils are shown in Table-2. The changes in the amount of available zinc are also shown graphically in Figs. 1 and 2.

TABLE 2—EFFECT OF VARIOUS TREATMENTS ON THE AVAILABILITY OF ZINC (PPM) IN SOIL

Treatments	K-soil			B-soil		
	Days of incubation			Days of incubation		
	1	7	30	1	7	30
$Zn_0P_0OM_0$	2.80	2.30	1.70	2.50	2.10	2.30
$Zn_0P_1OM_0$	3.50	2.40	1.80	2.70	2.20	2.70
$Zn_0P_2OM_0$	2.50	2.30	1.90	3.00	2.40	2.00
$Zn_0P_0OM_1$	5.30	2.80	2.20	3.40	2.60	4.10
$Zn_0P_1OM_1$	3.90	2.60	1.70	3.70	2.20	2.40
$Zn_0P_2OM_1$	6.00	3.10	2.90	4.30	2.60	2.50
$Zn_1P_0OM_0$	8.80	8.50	4.60	4.40	4.05	1.50
$Zn_1P_1OM_0$	13.50	5.20	1.80	4.50	4.95	2.10
$Zn_1P_2OM_0$	11.20	4.00	3.40	6.40	5.10	2.50
$Zn_1P_0OM_1$	7.50	6.50	3.60	8.50	3.50	1.20
$Zn_1P_1OM_1$	9.00	3.10	1.90	7.50	9.90	3.30
$Zn_1P_2OM_1$	6.00	4.00	3.30	6.00	10.30	2.70

It was found that there was an immediate increase in DTPA-extractable zinc in both native and Zn-treated

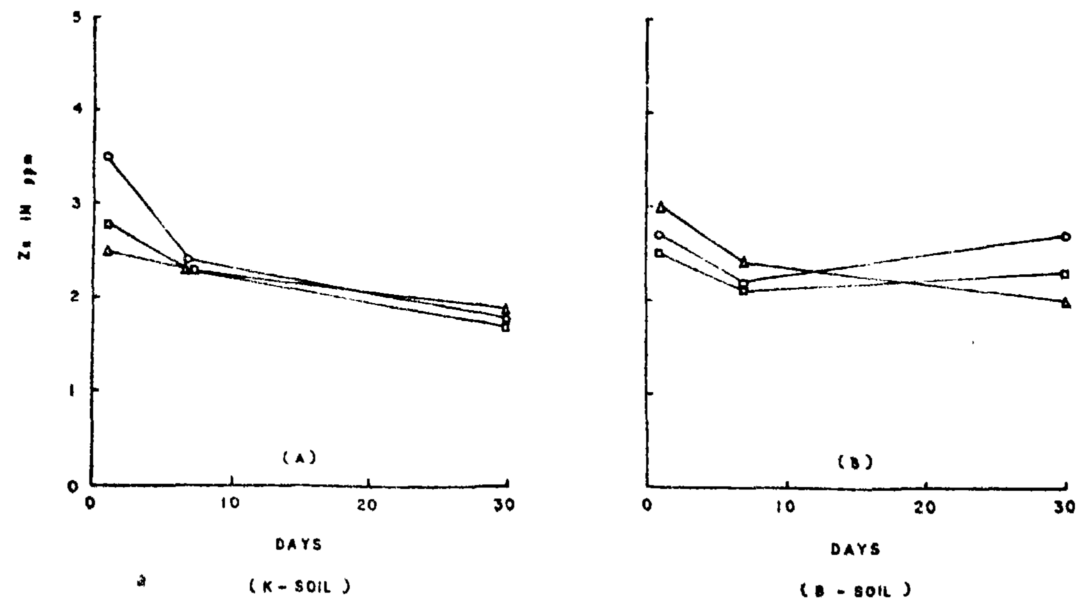


Fig 1. Effect of different levels of P on DTPA-extractable Zn in native soils

□ P_0 ○ P_1 △ P_2

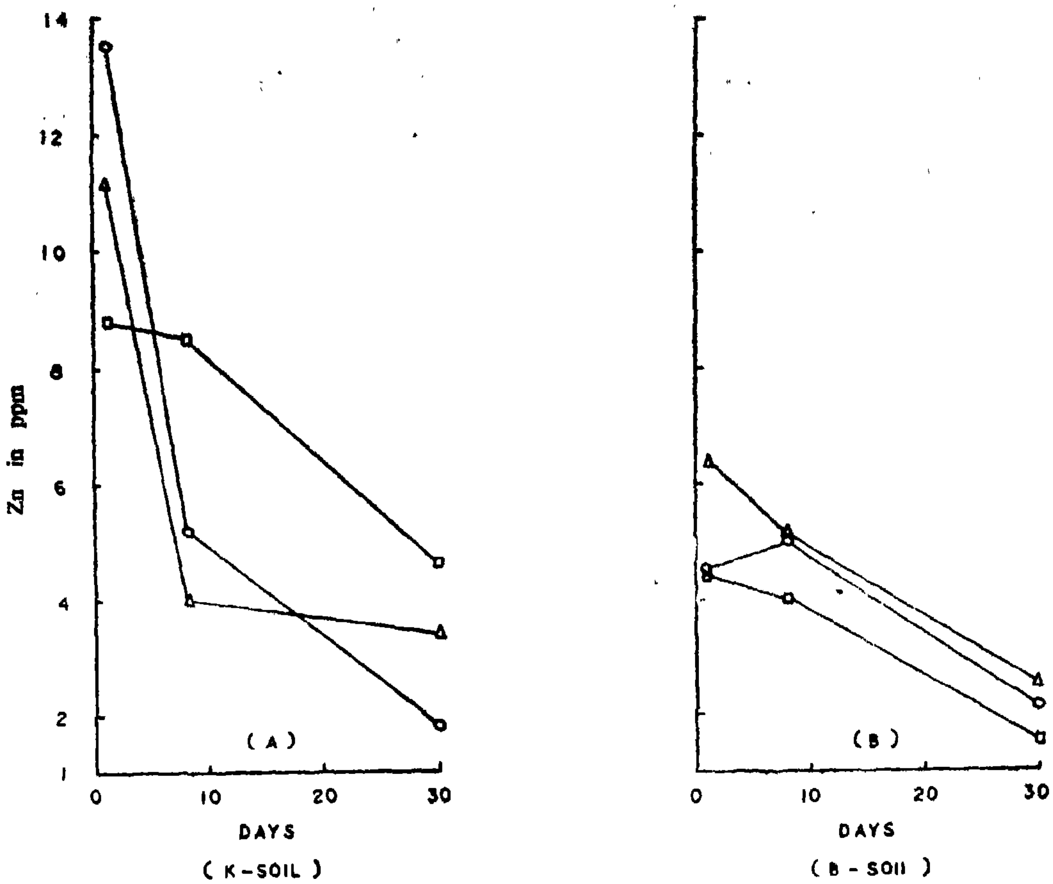


Fig. 2. Effect of different levels of P on DTPA-extractable Zn in Zn treated soils

□ P_0 ○ P_1 △ P_2

soils, especially when a lower dose (50 ppm P_2O_5) of phosphate was applied. The effect was more conspicuous in Kalyani soil (K-soil). In Burdwan soil (B-soil) however, even higher doses of applied phosphate caused an increase in available zinc. This may be due to lowering of *p*H associated with the addition of phosphate in the form of superphosphate. Laker[4] also reported that the application of high phosphate level increased the content of extractable zinc.

On incubation for 7 days, extractable zinc content was decreased in both the soils with higher doses of phosphate. This is obviously due to chemical precipitation as a result of increased *p*H and phosphate ion activity coupled with fixation in smectite dominated clay lattice.

On prolonging the period of incubation upto 30 days a further decrease was observed in all cases except the B-soil treated with lower dose of superphosphate. In comparison with the control series soil samples treated with higher dose of phosphate showed a smaller decrease in DTPA-extractable zinc. With Zn-treated soils, sharper decrease was observed in case of lower dose of applied phosphate.

It appears that on prolonging incubation while the applied phosphate does not alter much the available zinc status of the alluvial soils, most of the added fertilizer zinc is transformed into unavailable pool, especially when a lower dose of superphosphate is applied to the soil.

The effect of addition of organic matter as EDTA on zinc availability in soil is shown in Table 2 and changes in available zinc in the soils on incubation for different periods are shown graphically in Figs. 3 and 4.

It can be seen that on adding EDTA the DTPA-extractable Zn content immediately increases in both the phosphate treated soils. The effect was more pronounced in K-soil. In case of Zn-treated soil, however, while the B-soil showed a general increase, the K-soil exhibited a decreasing trend. The increase is due to mobilization of the less labile micronutrient pool through the chelating effect of EDTA. A somewhat similar observation was made by Elgawhary *et al*[5]. The decrease in extractable Zn is due to fixation of added zinc in the clay mineral lattice or immobilisation of the element as insoluble phosphates or basic

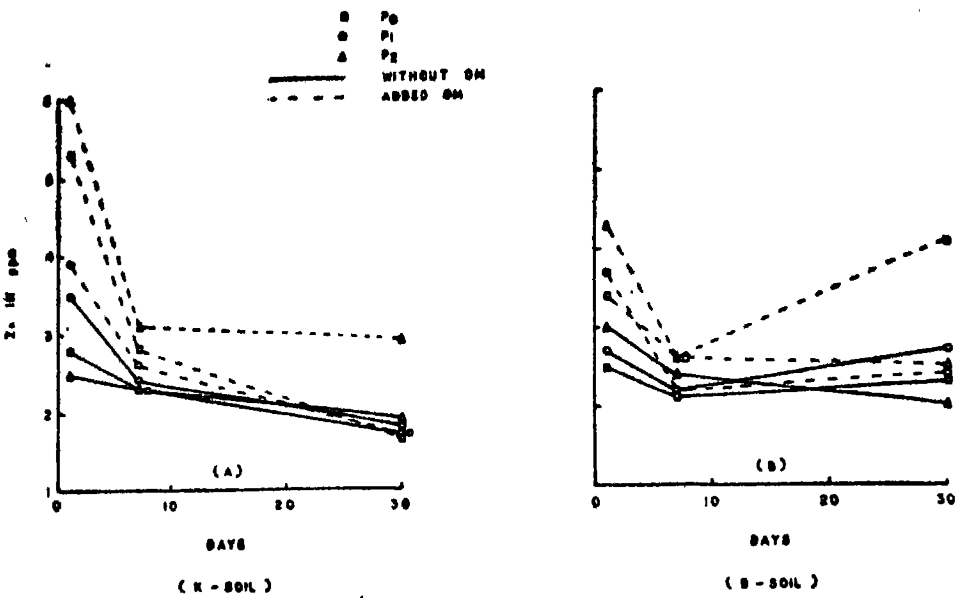


Fig. 3. Effect of OM and P on DTPA-extractable Zn in native soils

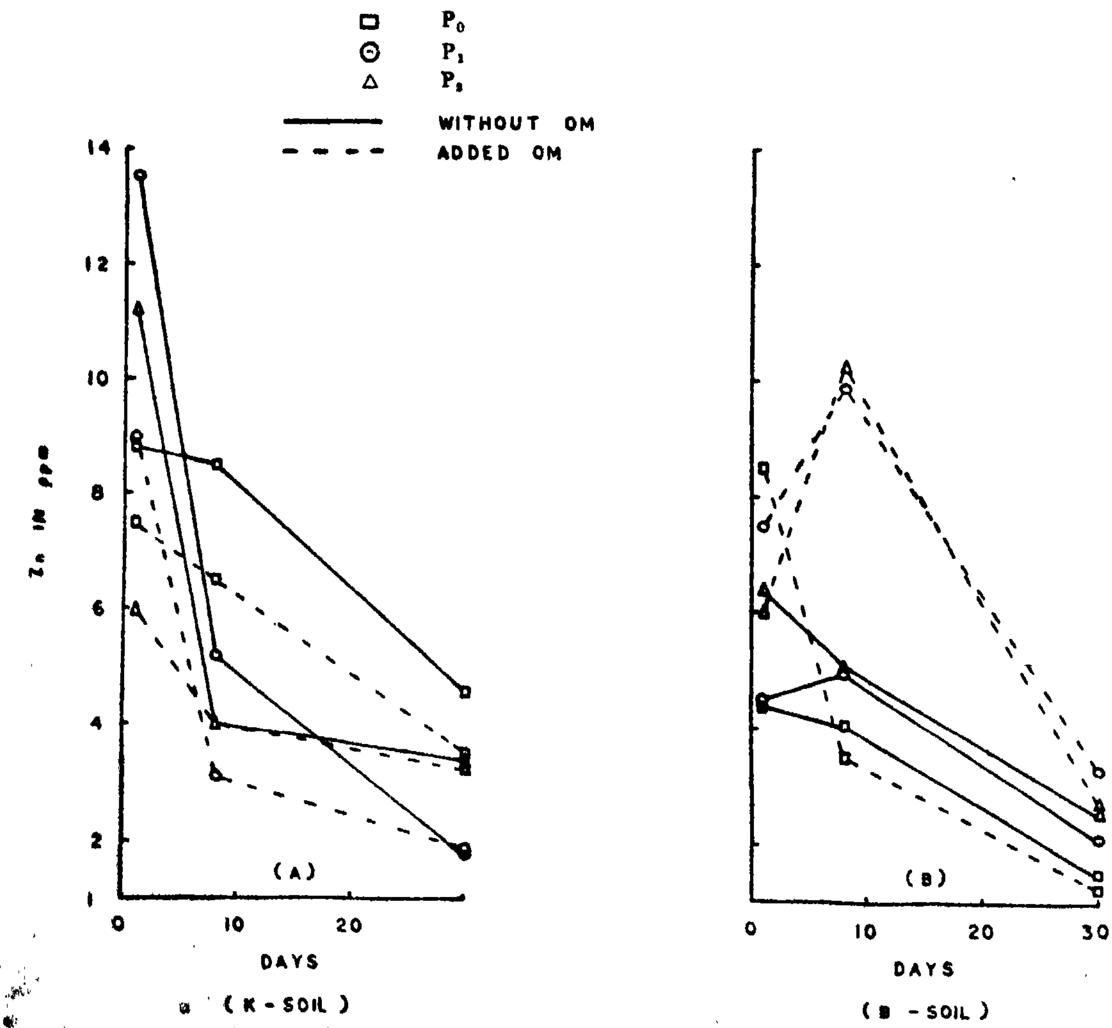


Fig. 4. Effect of OM and P on DTPA-extractable Zn in Zn treated soils

phosphates at the relatively higher *p*H of the soil in question.

On incubation for 7 days, a general decrease in DTPA-extractable Zn was noticed in all cases, particularly when no Zn-fertilizer was added. In case of Zn-treated and phosphate fertilized B-soil, however, an increase in extractable Zn content was observed. The decrease may be due to conversion of Zn-EDTA complex to more stable Fe^{III}-EDTA complex with the resulting immobilization of soluble zinc as shown below :

$$\left.\begin{array}{l} Fe_2O_3.xH_2O, \\ Fe^{III}\text{-phosphate} \end{array}\right| + \text{Zn-EDTA} \rightleftharpoons Fe^{III}\text{-EDTA} \quad \begin{array}{r} ZnO.yH_2O, \\ +\text{Zn-phosphate} \end{array}$$

Since EDTA is somewhat resistant to decomposition at a relatively higher *p*H the above general reaction proceeds towards the right hand side. At a lower *p*H, however, more zinc is mobilized from the non-labile pool which causes an increase in available zinc.

On prolonging incubation, extractable zinc status was decreased in all soil samples. This is obviously due to chemical or microbial decomposition of EDTA and the reaction of the type shown above resulting in the fixation of labile zinc. Both the native and zinc treated soils were found to behave in a similar manner even under the phosphate fertilized conditions.

References

1. W. L. LINDSAY and W. A. NORVELL, *Agron. Abs.*, 1969, p. 84.
2. A. K. MANDAL and B. DAS, *J. Indian Chem. Soc.*, 1978, 55, 93.
3. C. A. BLACK, Methods of Soil Analysis, Part-2, Amer. Soc. Agro. Inc., Madison, Wisconsin, USA. 1965.
4. M. C. LAKER, *S. Afr. J. Agric. Sci.*, 1967, 10, 323-330.
5. S. M. ELGAWHARY, W. L. LINDSAY and W. D. KEMPER, *S. S. Soc. Amer. Proc.*, 1970, 34, 66-70.

J. Indian Chem. Soc.,
Vol. LVII, February 1980, pp. 186-187

The Interaction of Gelatin Molecule with Molybdate Ions

J. P. S. ARORA, R. P. SINGH, D. S. JADON* and S. K. MITTAL

Chemistry Department, D.A.V. College, Muzaffarnagar (U.P.)

Manuscript received 10 October 1979, accepted 9 January 1980

The interaction of simple tetrahedral oxoanion MoO_4^{-2} has been studied with gelatin using polarographic (pH 5.57) and equilibrium dialysis techniques at two different temparatures. The apparent intrinsic constant and the average maximum binding sites have been calculated with the help of Scatchard's plots. The values of association constants (log K) have been found to be 3.574 (pH 5.57), 3·563 (pH 7.50) and 3.522 (pH 5 30) at lower temperature while 3.535, 3.522 and 3.477 respectively at higher temperature. The binding sites are suggested to be non-identical at pH 5.57 and 7.50 while identical at pH 9.30. Tho number of binding sites available for interaction with the molybdate ion is much less than the actual number of cationic groups i.e. 16, 15 and 12 at lower temperature and 14, 11 and 10 at higher temperature, at pH values 5.57, 7 50 and 9.30 respectively. The values of free energy changes were found to be −4·649, −4·635 and −4.581 at 10° while −4.842, −4.797 and −4.763 Kcal/mole at 25°, respectively. The values of enthalpy changes were found to be in increasing order. The order of binding parameters and thermodynamic constants suggested that the interaction is pH and temperature dependent. Statistical effects seem to be more pronounced at lower while the electrostatics are at higher molybdate concentration.

THE role of molybdenum in catalysing the biological activity of enzymes[1] and in accelerating the formation of amino acids in plants[2] is well known. The electron paramagnetic resonance and other studies have been carried out by several workers to confirm its association with the electron transfer process of many enzymes[3-8]. Such studies have revealed that molybdenum forms the active constituent of enzymes like other transitional elements in the metalloproteins. Several studies have also been made on model-compounds in order to show the type of bonding in enzymes[9-11]. In most of these investigations the thiol groups of enzymes have been shown to be involved.

The existence of molybdenum(VI) as a cation appears to be unlikely, presumably, on account of its complex polymerisation reactions giving highly charged anionic species[12] in acidic solutions. However, Chojnacka[13] has reported the existence of a simple tetrahedral oxoanion (MoO_4^{-2}) above pH 5.0. In fact the reactions of oxyacids of molybdenum with proteins may provide a means for their isolation. The formation of rubber like polymers between polyacid of molybdenum and gelatin has been reported by Kumar and Sinha[14]. Various physico-chemical methods used for the investigation of metal-protein systems have also been employed by Malik *et al.*[15-16] to study the binding of molybdate ions above and below the isoelectric points of fibrillar and globular proteins. In these studies the binding was found to be pH and concentration dependent. Recently they have made a detailed investigation on the binding of molybdenum(VI) with modified and denatured ovalbumin using polarographic and equilibrium dialysis methods[17]. These workers have also proved the general applicability of pH-metric method to investigate the polyacid-protein systems[18-19]. Comparative molybdate binding studies of ovalbumin-s heat and alkali denatured ovalbumin have also been made in the soluble[20] and insoluble range[21] employing appropriate methods. The results below isoelectric point have been interpreted in terms of the protein denaturation. In the present paper, the results on the binding of molybdenum with gelatin employing polarographic and equilibrium dialysis methods have been reported. The effect of pH, temperature and molybdate concentration on the binding parameters are also discussed.

Experimental

Protein :

The solution of gelatin (Oxoid, London) was prepared in deionized double-distilled water at 60°. This solution was dialysed in a cellophane bag against distilled water to obtain an isoionic solution. The solution was centrifuged and its concentration was determined by drying a known aliquot in an air oven at 105-110°.

Reagents :

Ammonium molybdate (E. Merck) was dissolved in doubly distilled water and estimated gravimetrically by the oxine method[22]. Sodium acetate (0.2*N*) and acetic acid (0.5*N*), both B.D.H., were used for the preparation of acetate buffer, 1.0 *M* ammonium chloride and 1.0 *M* ammonia were used for the preparation of buffers of higher pH values. 1.0 *M* potassium chloride (B. D. H.) solution was used for the adjustment of ionic strength.

Techniques :

*p*H-measurements : The *p*H-values of acetate and ammonia-ammonium chloride buffers were measured

*For correspondence

using a systronic pH-meter. Potassium hydrogen phthalate buffer (pH, 4.0) and borax buffer (pH. 9.20) were used for standaridization of the instrument. For pH-measurements gelatin, molybdate and gelatin-molybdate mixtures were mixed with 0.0861 M HCl or 0.0605 KOH, the total volume was made upto 15 ml by adding double-distilled water and 1.0 M KCl for the adjustment of ionic strength (0.15). Purified nitrogen was passed through the mixtures, in order to ensure inert atmosphere, before making pH measurements.

Dialysis experiments: In equilibrium dialysis a solution of known protein concentration (5.0 gm/L) at the desired ionic strength (0.15) in KCl was placed inside an 23/32" visking cellophane bag which had been thoroughly rinsed and finally soaked in KCl solution at the desired ionic strength. The bag was inserted in a glass stoppered tube containing the 'out side' solution of KCl and molybdate ion. The desired pH of 'inside' and 'outside' solution was maintained with the help of suitable buffers (5.57, 7.50 and 9.30). Several similar sets of solutions having fixed 'inside' gelatin and different 'outside' molybdate solutions (total volume 5.0 ml. inside and outside) were prepared. The tubes were shaken at 10 and 25° for a time just sufficient to attain the equilibrium. The outside solution was then separated and analysed for its molybdenum concentration[23].

When no precipitation occurred, V_m, the average number of molybdenum bound per 10^5 gm of gelatin, could be calculated directly as follows :

$$V_m = \frac{Mo_T - Mo_F}{(P)}$$

where Mo_T and Mo_F represent the total and free concentration of molybdenum and (P) is equal to the total molar concentration of the protein. Control studies indicated that molybdenum binding by the tubing was essentially negligible, but a small loss of gelatin always occurred when the tubing was tied off, and the initial volume of the protein was always less than the outside solution. Results are reported at three different pH-values (5.57, 7.50 and 9.30).

Diffusion current measurements: These measurements were carried out on a Heyrovsky polarograph Model LP55 in conjunction with a Pye Scalamp galvanometer in the external circuit. An H-shaped polarographic cell as recommended by Tanford[24] was used. Purified nitrogen was bubbled through the mixtures and triple distilled mercury was used for dropping mercury electrode. The cell was immersed in a water thermostat at 25±0.1°. The capillary used, had a flow rate of about 2.2 mg./sec. with a drop time of 3.5 seconds. The rate of flow of mercury drops was determined by Lingane's method[25]. Since the capillary characteristics (m,t) have a marked effect on diffusion current (which is directly proportional to $m^{2/3}$ $t^{1/6}$), these factors were, therefore, controlled carefully throughout these experiments.

The following sets of mixtures were prepared for diffusion current measurements :

(i) Different concentrations of gelatin (0.25-2.25%) were taken in pyrex tubes and 2.5 ml of 0.004 M ammonium-molybdate solution was added in each case. The total volume was made to 12.0 ml by adding fixed amount of buffer and requisite amount of water and 1.0M KCl solution to adjust ionic strength at 0.15. The results are given in Fig. 1A in the form of percentage-protein against id/(id)$_0$.

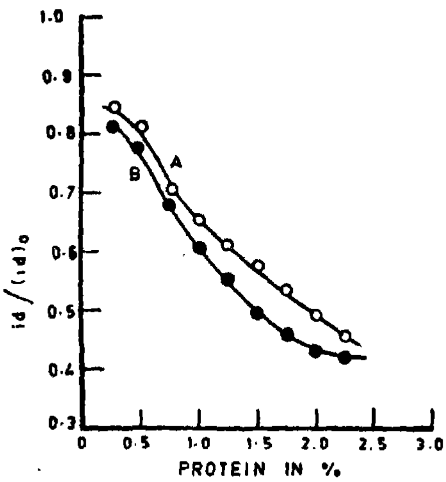


Fig. 1 A & B. Plots of id/(id)$_0$ vs. protein concentration at pH 5.57. Curves A and B are for 8.33×$10^{-4}$$M$ and 6.66×$10^{-4}$$M$ molybdate concentrations respectively.

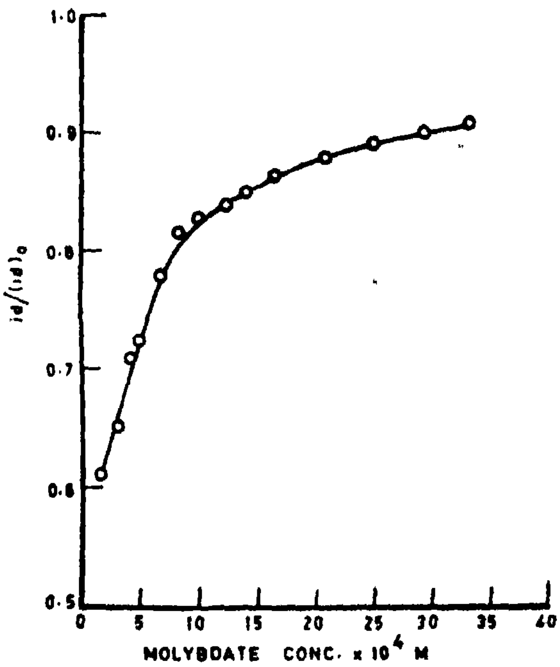


Fig. 1C. Plot of $id/(id)_0$ vs. molybdate concentration for varying concentrations of molybdate and protein fixed at pH 5.57.

(ii) Varying concentrations of gelatin and $6.66 \times 10^{-4} M$ ammonium molybdate were taken in 12.0 ml at an ionic strength of 0.15. Fig. 1B shows the variation of $id/(id)_0$ against protein concentration.

(iii) Varying concentrations of ammonium molybdate ($1.33 \times 10^{-4} M$ to $33.3 \times 10^{-4} M$) were mixed with 5.0 gm/litre of gelatin in each case. The total volume was kept 12.0 ml by adding fixed amount of buffer and requisite amount of water and 1.0 *M* KCl to adjust ionic strength at 0.15. The variation of diffusion current ratio with total molybdate ion concentration has been shown in Fig. 1C.

Results and Discussion

Diffusion current

The protein would normally affect both the half-wave potential ($E_{1/2}$) and diffusion current (id) of the reduction wave of the metal ion[24]. In this case no shift in $E_{1/2}$ of the molybdenum(VI) in presence of gelatin was observed. Tanford's method[26], based on the variation of the ratio of $id/(id)_0$ could be applied satisfactorily at *p*H 5.57. The marked decrease in the diffusion current at *p*H 5.57 as determined experimentally and shown in Fig. 1 and 2 (for sets (i) and (ii)) provides sufficient information regarding the binding of Mo(VI) to gelatin. Similar type of decrease in the diffusion current of the dyes and molybdate anions in the presence of proteins was observed by Malik *et al.*[16,17,27], hence the reduction in the diffusion current of Mo(VI) in the presence of increasing amount of gelatin must be ascribed due to interaction, These findings are in agreement to Tanford[24], who believed that when a reducible substance was bound to a protein there is a reduction in the diffusion current and this decrease may be used to calculate the binding constants.

If id and $(id)_0$ are the diffusion currents of molybdenum in the presence and absence of gelatin respectively and Co, C_F and C_B the concentrations of total, free and bound molybdenum respectively, then the molar concentration of bound molybdenum to protein can be evaluated with the help of following equations :

$$C_O = C_F + C_B$$

$$id/(id)_O = (C_F + k\ C_B)/C_O$$

$$\text{and } C_B = (C_O - id/(id)_O\ C_O)/1\text{-}k$$

where k (the fractional coefficient) is the limiting value of $id/(id)_O$ when so much protein has been added that all the molybdenum is protein bound. The value of k is obtained by an extrapolation method

$$id/(id)_O = k$$

$$\lim_{C_F \to O}$$

In our studies the value of k was found to be 0.41 from Figs. 1A and 1B at *p*H 5.57. Figs. 1A and 1C show sharp breaks with rising concentration of protein or molybdenum(VI). It may be seen that the addition of gradually increasing amount of gelatin results in the reduction of diffusion current of Mo(VI) till it attains a limiting value (k). Constancy in diffusion current indicates complete binding of molybdenum to gelatin.

The data were analysed by means of Scatchard's equation[28-30]

$$V_m/C_F = K_n - KV_m$$

the value of V_m (average mole of molybdenum bound per 10^5 gm of gelatin) is determined by the relation, $V_m = C_B/P$, where P and C_B have their usual meanings. K is the average apparent association constant for the binding at each site and n is the average maximal number of binding sites on gelatin with the same association constant(K). If all the binding sites are equivalent and independent, a plot of V_m/C_F as a function of V_m should give a straight line such that the intercept on the V_m/C_F axis is K_n, as V_m approaches zero as a limit, and the intercept on the V_m axis is n, as V_m/C_F approaches zero as a limit. Deviation from linearity occurs when binding takes place at more than one set of sites with different association constants[28-31]. The contribution of electrostatic factors to the interaction[28-32] or the change in ionic species of reacting species may also produce curvature.

The results obtained are shown in Fig. 2. A linear relationship does not exist between V_m/C_F and V_m. In fact, the Scatchard's plot of the data shows two straight line regions which indicate more than one class of sites[30]. The intercept of the upper part with the abscissa in Fig 2 yields a value of $n_1 = 6$, for the number of binding sites in the first class ; corresponding the slope-K_1, gives the binding constant $K_1 = 0.86 \times 10^4$. To determine the number of sites in the second class and their binding constants, we plot V'_m/C_F Vs V'_m where $V'_m = V_m$ − no. of primary sites, for the results at *p*H 5.57. This procedure subtracts out the contribution of the primary sites to the data. This is valid when the two classes of sites does not affect binding at the other. This seems to be the case here. From Fig. 3 we obtain $n_2 = 2.5$ and $K_2 = 0.38 \times 10^4$ for the second class of sites. Again, the deviation of points above $V_m = 2.5$ is either due to a consequence of the change in ionic species of molybdenum[34] or due to the involvement of the third class of sites in the interaction. It is not surprising since the dissociation of a weak acid (here molybdic acid) is *p*H and concentration dependent and is thus a subject of electrostatic effects such as that operative in ampholytes at varying *p*H. Assuming that there are additional third class of sites then from Fig. 4, the remaining $n_3 = 45$ sites may belong to the most weaker sites with $K_3 = 0.05 \times 10^4$. These valves of different classes of sites along with their association constants as determined from polarographic data are compiled in Table 1. The smaller number of sites found from the experimental data clearly indicates that only a few groups participate in

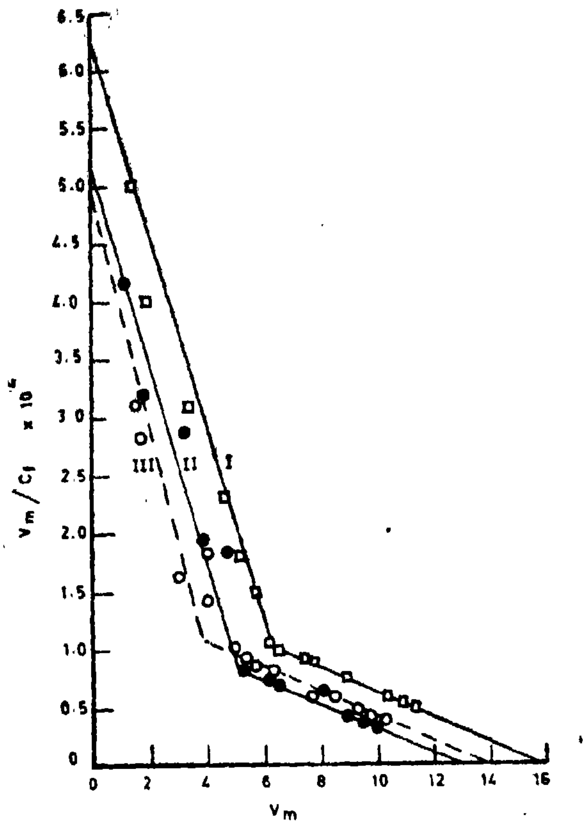


Fig. 2. Plots of V_m/C_f vs. V_m for molybdate-gelatin system at *p*H 5.57. Curves I, II & III are for equilibrium dialysis at 10°, polarography at 25° and equilibrium dialysis at 25° techniques respectively.

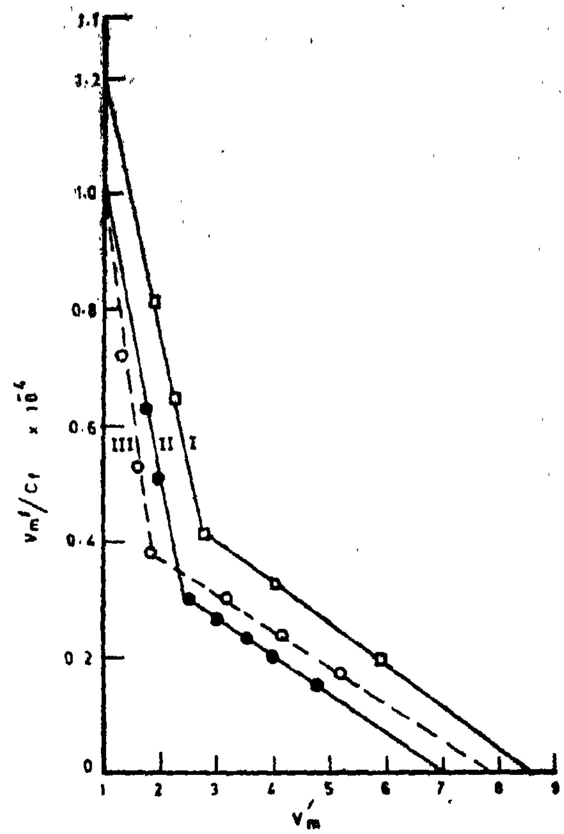


Fig. 3. Plots of V'_m/C_f vs. V'_m for molybdate-gelatin system at *p*H 5.57. Curves I, II & III are same as in Fig. 2.

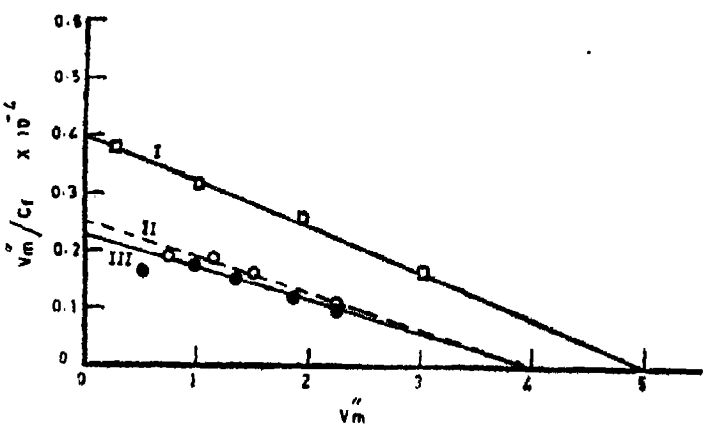


Fig. 4. Plots of V''_m/C_f vs. V''_m for molybdate-gelatin system. Curves I, II & III are same as in Fig. 2.

TABLE 1—THE VALUES OF BINDING CONSTANT FOR Mo(VI) WITH GELATIN

pH	Technique	Temperature 10°C								Temperature 25°C							
		n	n_1	n_2	n_3	LogK	$LogK_1$	$LogK_2$	$LogK_3$	n	n_1	n_2	n_3	LogK	$LogK_1$	$LogK_2$	$LogK_3$
5.57	Equilibrium dialysis	16	9	3.7	5	3.574	3.954	3.477	2.819	14	6	2.5	5	3.535	3.919	3.602	2.803
5.57	Polarography	—	—	—	—	—	—	—	—	13	6	3	4	3.584	3.933	3.547	2.792
7.50	Equilibrium dialysis	15	8	5	—	3.563	3.837	3.041	—	11	6.4	4	—	3.522	3.732	3.000	—
9.30	Equilibrium dialysis	12	7	4	—	3.522	3.808	3.041	—	10	6.2	3	—	3.477	3.681	2.903	—

molybdate-gelatin interaction, since the actual number of cationic sites is 87 for 10^5 g.m. of gelatin[35]. Further information about the nature of the binding was obtained from equilibrium dialysis experiments where it was possible to work at *p*H-values other than 5.57.

Equilibrium dialysis.

The results obtained at three different *p*H-values (5.57, 7.50 and 9.30) and at two temperatures (10 and 25°) are expressed graphically (Figs. 2 to 6) as in the case of polarographic method. The association constants and binding sites calculated from Scatchard's plots are compiled in Table 1. Although these constants at *p*H 5.57 compare favourably by both the methods, yet the values from polarography was found to be somewhat different from that obtained by equilibrium dialysis. This slight difference is understandable in view of the fact that equilibrium dialysis generally has been accepted as reliable and accurate method for the determination of binding between small molecules and proteins. This can also be explained by the fact that in equilibrium dialysis more time is given for equilibrium while in polarography observations were taken immediately after preparing the gelatin-molybdate mixtures.

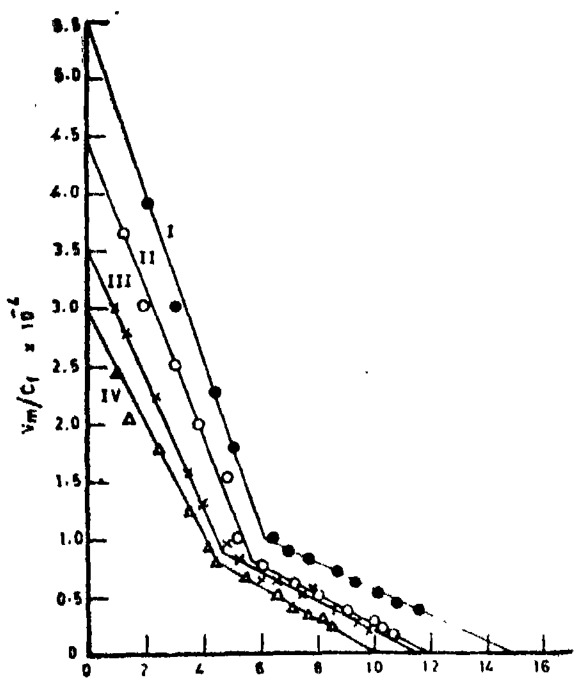


Fig. 5. Plots of V_m/C_f vs. V_m for molybdate-gelatin system by equilibrium dialysis technique. Curves I, II, III & IV are for *p*H 7.50 (10°), *p*H 9.30(10°), *p*H 7.50 (25°) and *p*H 9.30 (25°) respectively.

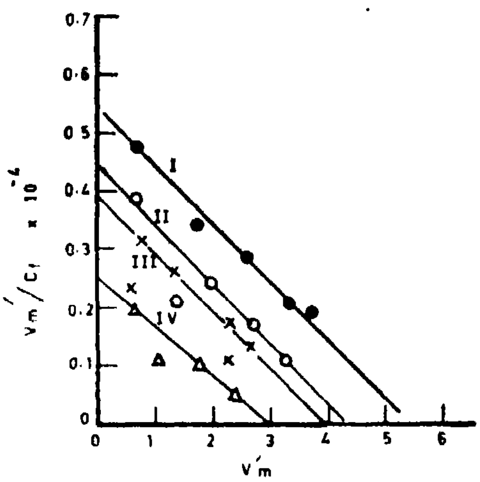


Fig. 6. Plots of V'_m/C_f vs. V'_m for molybdate-gelatin system by equilibrium dialysis technique. Curves I, II, III & IV are same as in Fig. 5.

From *p*H 5.57 to 9.30 a non-linear relationship exists between V_m/C_f and V_m plot and the extrapolation to V_m/C_f (Kn) and the V_m axis (n) are shown in figure 5. The values of binding constants are given in Table 1. The fact that the relationship between V_m/C_f vs. V_m is linear over the range of Mo(VI) concentration studied indicates that a second class of binding sites if it exists at *p*H 9.30 must have a much smaller association constant than that observed for the primary binding sites (Table 1). A comparison of the binding constants at different *p*H-values indicates that the

interaction is highly pH dependent. It is considered likely that free cationic grouped on the gelatin molecule may be the primary binding sites[28-30]. It may also be inferred that the difference in pk values of the molybdic acid and the reactive cationic groups may account, atleast in part, for the difference in binding behaviour.

The various thermodynamic perameters i.e., free energy change ($\triangle G^\circ$), enthalpy change ($\triangle H^\circ$) and entropy change ($\triangle S^\circ$) for the binding have been calculated by the standard thermodynamic procedures. These values are given in table 2. The order of $\triangle G^\circ$ values are in agreement with decreasing positive charge and increasing negative charge on protein molecule. The values for enthalpy changes are found to be -1.008, -1.060 and 1.163 Kcal/mole at pH values 5.57, 7.50 and 9.30 which suggested a stronger combination at higher pH than at lower pH. The relationship between binding and pH indicates that the net charge on protein molecule has great influence on anion protein interaction. Similarly a change of temperature brings change in the binding capacity which may be attributed due to structural changes in protein molecule.

Evidence of interaction from the titration curves of gelatin with molybdate :

The isoionic gelatin was titrated in the presence and absence of molybdate using standard hydrochloric acid and potassium hydroxide solutions respectively. The curves are shown in the form of volume of acid or alkali added vs. pH-values of the resulting mixtures (Fig. 7). These curves of protein, molybdate and mixture are quite apart, hence valuable information regarding the interaction was gained. There was precipitation below the isoelectric point of gelatin, hence more hydrogen ions were consumed, most probably due

TABLE 2—BINDING CONSTANTS AND THERMODYNAMIC PARAMETERS OF Mo(VI)-GELATIN SYSTEM

pH	Technique	Temperature 10°C n	LogK	$\triangle G^\circ$ Kcal/mole	$\triangle H^\circ$ Kcal/mole	$\triangle S^\circ$ Cal/deg./mole.	Temperature 25°C n	LogK	$\triangle G^\circ$ Kcal/mole	$\triangle S^\circ$ Cal/deg./mole.
5.57	Equilibrium dialysis	16	3.574	−4.649	−1.008	+12.85	14	3.535	−4.842	+12.86
5.57	Polarography	—	—	—	—	—	13	3.584	−4.910	—
7.50	Equilibrium dialysis	15	3.563	−4.635	−1.060	+12.63	11	3.522	−4.797	+12.20
9.30	Equilibrium dialysis	12	3.522	−4.581	−1.163	+12.07	10	3.477	−4.763	+12.07

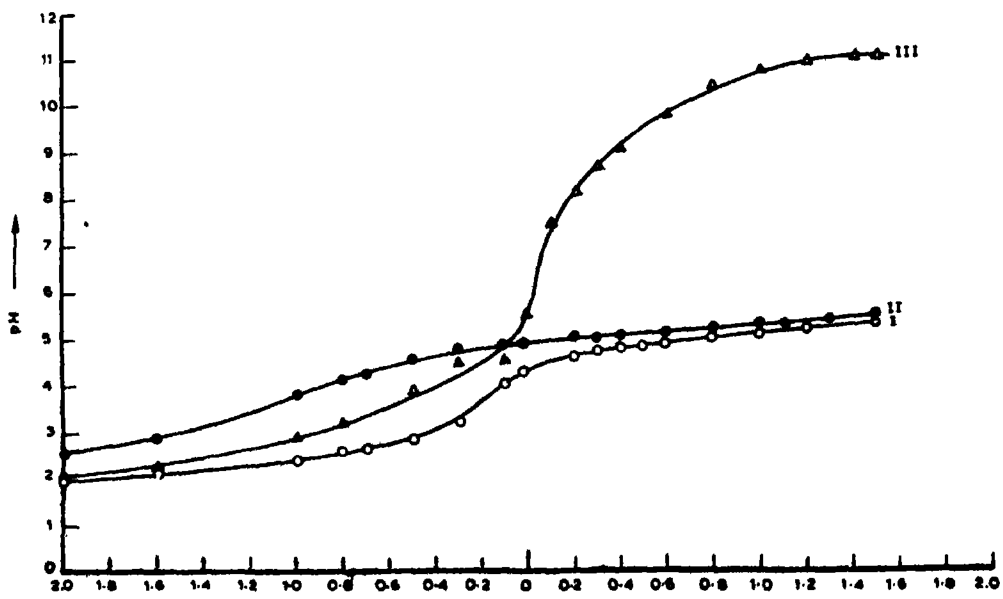


Fig. 7. Plots of pH vs. volumes of HCl or KOH added. Curves I, II & III are for $1.0\times10^{-3}M$ molybdate, $1.0\times10^{-3}M$ molybdate+0.6% gelatin and 0.6% gelatin respectively.

to the formation of poly-nuclear complexes, as was suggested by Malik and Arora[16] in the interaction of molybdenum with proteins. Some useful information has also been gained from the curves of $\triangle pH$ vs. pH or the vol. of HCl or alkali as well as from $\triangle pH/\triangle V$ against the volume of acid or alkali added (Fig. 8). The $\triangle pH$ of molybdate + protein molybdate vs. the volume or pH of molybdate – protein mixtures (Fig. 9) indicated that the change was minimum near the

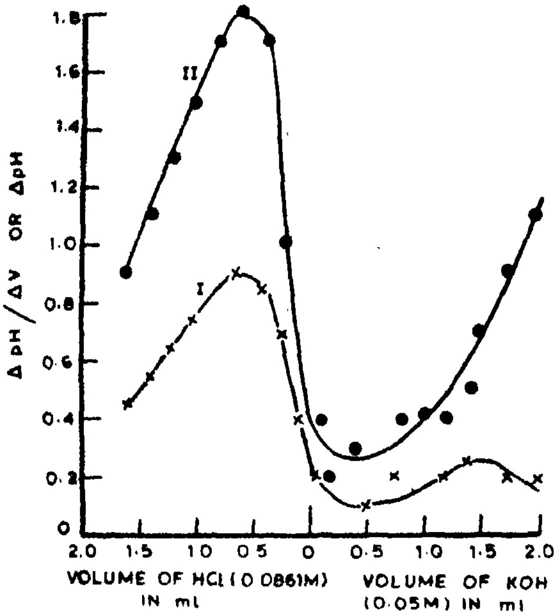


Fig. 8. Plots of $\triangle pH/\triangle V$ or $\triangle pH$ vs. volumes of HCl or KOH added. Curves I & II are for $\triangle_{\phi}H/\triangle V$ and pH for molybdate-gelatin system respectively.

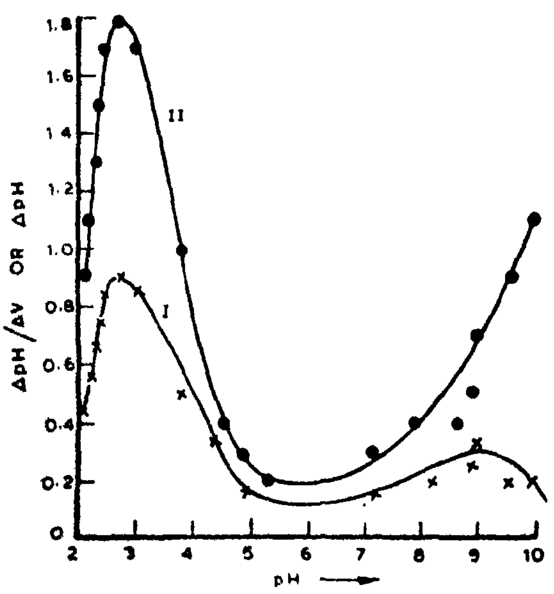


Fig. 9. Plots of $\triangle pH/\triangle V$ or $\triangle pH$ vs. pH for molybdate-gelatin system. Curves I & II are same as in Fig. 8.

isoelectric point while it increased upto pH 9.50 and then decreased. These results also go to show that the complexation of molybdate ion takes place upto pH 8.50 and then decreases.

The appearance of maxima at pH 2.80-3.00 in the $\triangle pH$ vs. pH curve is similar to the observed in the pH vs. log transmittance curve of molybdate-gelatin mixture[16]. This indicates a change of the isoelectric point as well as the point of maximum interaction. On both the sides the abrupt decrease pointed to a change of the ionic species of molybdenum. It is difficult to correlate pH-metric results with those obtained from the polarographic and equilibrium dialysis technique.

From the results obtained different tentative hypotheses can be made regarding the molybdate-protein interaction. The pH-dependent binding constants suggest that cationic sites are the chief sites for binding the anions. Protein deprotonation and enhanced negative charge would cause such pH-dependent results. The persistence of binding at pH 9.30 may be attributed to the guanidinium groups of arginine residues which have a higher value of ionisation constant (pk > 12). The total number of binding sites (n) at two temperatures show that all the positive groups are not available for combination. The small number of binding sites thus does not allow us to determine which groups (arginine, lysine or imidazole) are involved in binding with molybdate. These findings are in agreement with those earlier obtained by Malik *et al.*[15] in the interaction of molybdate ions with transfusion gelatin and ovalbumin. Similar type of conclusions were drawn by Craig *et al.*[37] in the interaction of ovalbumin with chloroaurate ions below the isoelectric point of the protein.

Our pH dependent result between Mo(VI) and gelatin could thus be explained by assuming an interaction with the positively charged groups. The complex formation between Mo(VI) and histidine[38] as well as guanidine[39] further goes to support our results in lower pH range. Towards higher pH the decreased binding may be due to deprotonation of the imidazolium and amino groups while guanidinium groups remained protonated (pK > 12). However, owing to the complexity of the macromolecular system it is difficult to find out the exact groups which are involved in Mo(VI)-gelatin reaction.

References

1. D. A. RICHERT and W. W. WESTERFELD, *J. Biol. Chem.*, 1954, 209, 179.
2. J. BERDUCOU and R. MACHE, *Compt. Rend.*, 1963, 257, 229.
3. G. NAKOS and L. E. MORTENSEN, *Biochem.*, 1971, 10, 455.
4. H. DALTON, J. A. MORRIS, M. A. WARD and L. E. MORTENSEN, *Biochem.*, 1971, 10, 2066.
5. A. NASON, *Bacteriol. Rev.*, 1962, 26, 16.

6. G. A. HAUSKA, R. E. MCCARTY, R. J. BERZBORN and E. RACKER, *J. Biol. Chem.*, 1971, **246**, 3524.

7. R. C. BRAY and T. VINNGARD, *Biochem. J.*, 1969, **114**, 725.

8. R. C. BRAY, G. PALMER and H. BEINERT, *J. Biol. Chem.*, 1964, **239**, 2667.

9. P. SPIVACK, A. P. GAUCHAN and Z. DORI, *J. Amer. Chem. Soc.*, 1971, **93**,

10. J. T. SPENCE, *Coord. Chem. Rev.*, 1969, 4, 475.

11. G. CLOVOS and J. T. SPENCE, *Biochemistry*, 1972, **11**, 2542.

12. "Advances in the Chemistry of the Co-ordination Compounds" edited by S. KRISCHNER, Macmillan, New York, 1961, p. 67.

13. J. CHOJNACKA, *Rocznik, Chem.*, 1963, 37, 259.

14. S. KUMAR and B. C. SINHA, *J. Soil. Ind. Research (India)*, 1961, **20B**, 359.

15. W. U. MALIK and J. P. S. ARORA, *J. Electroanal Chem.*, 1969, **22**, 359.

16. W. U. MALIK and J. P. SINGH ARORA, *J. Electroanal Chem.*, 1970, **26**, 414.

17. W. U. MALIK, J. P. S. ARORA, D. S. JADON, R. P. SINGH, K. K. SHARMA and R. S. MALIK, *J. Electroanal Chem.* (Communicated).

18. W. U. MALIK, J. P. S. ARORA and R. P. SINGH, *J. Indian Chem. Soc.* (accepted).

19. J. P. S. ARORA, R. P. SINGH and D. S. JADON, *J. Studia Biophysica* (Communicated).

20. W. U. MALIK, J. P. S. ARORA and R. P. SINGH, *J. Biol. Chem.* (Communicated).

21. J. P. S. ARORA, R. P. SINGH and D. S. JADON, *J. Indian Chem Soc.* (Communicated).

22. A. I. VOGEL, "A Text Book of Quantitative Inorganic Analysis". Longmans, Green and Co. Ltd. London, 1961, p. 508.

23. F. WILL (III) and J. H. YO, *Anal. Chem.*, 1953, **25**, 1363.

24. C. TANFORD, *J. Amer. Chem. Soc.*. 1951, **73**, 2066.

25. I. M. KOLTHOFF and J. J. LINGANE, "Polarography", Interscience Publishers, Inc, New York, 1952, p. 214.

26. C. TANFORD, *J. Amer. Chem. Soc.*, 1952, **74**, 211.

27. W. U. MALIK and S. AHMED, *J. Electroanal. Chem.*, 1973, **47**, 155.

28. G. SCATCHARD, *Ann. N. Y. Acad. Sci.*, 1949, **51**, 660.

29. G. SCATCHARD, W. L. HUGHES (JR.) F. R. N. GURD and P. E. WILCOX, "Memrois of the University Laboratory of Physical Chemistry Related to Medicine and Public Health" Harvard University No. 3 Chemical Specificity in Biological Interaction, Acad. Press, Inc., New York (1954).

30. I. M. KLOTZ, "The Proteins". (Eds). H. NEURATH and K. BAILEY, Acad. Press. Inc., New York, 1953, Vol. 1, p-727.

31. F. KARUSH, *J. Amer. Chem. Soc.*, 1951, **73**, 1246.

32. G. SCATCHARD, J. S. COLEMAN and A. L. SHEN, *J. Amer. Chem. Soc.*, 1957, **79**, 19.

33. N. D. CHASTEEN and J. FRANCAVILLA, *J. Phys. Chem.*, 1976, **80**, 867.

34. K. KUSTEN and S. T. LIU, *J. Amer. Chem, Soc.*, 1973, **95**, 2487.

P. F. KNOWLES and H. DIEBLER, *Trans. Faraday Soc.*, 1968, **64**, 977.

H. DIEBLER and R. B. TIMMES, *J. Chem. Soc.*, 1971, A-273.

35. A. C. CHIBNALL, *J. Intern Soc. Leather Trades Chemist*, 1946, **30**, 1.

36. I. M. KLOTZ, In "The Proteins". (Eds) H. NEURATH and K. BAILEY, Acad. Press, Inc. New York, 1953, Vol. 1, p-227.

37. J. P. CRAIG (JR.), A. G. GARRETT and H. B. WILLIAMS, *J. Amer. Chem. Soc.*, 1954, **76**, 1570.

38. J. T. SPENCE and J. Y. LEE, *Inorg. Chem.*, 1965, **4**, 385.

39. V. I. SPITOYN and M. P. RUBBEL, *Zhur. Neorn. Khim.*, 1962, **51**, 292.

J. Indian Chem. Soc.,
Vol. LVII, February 1980, pp. 188-190

Studies on the Fixation of Ammonium and Phosphate Ions as Influenced by Organic Matter and Free Oxides of Iron and Aluminium

S. K. BANERJEE

Dept. of Agril. Chemistry and Soil Science, Bidhan Chandra Krishi Viswa Vidyalay, Kalyani, Nadia

and

M. SENGUPTA and S. K. GUPTA

University College of Agriculture, Calcutta University

Manuscript received 14 September 1977, accepted 9 January 1980

The effect of organic matter and free oxides of iron and aluminium on the fixation of ammonium and phosphate ions in some soils of West Bengal has been studied. Ammonium fixation decreased and phosphate fixation increased in the organic matter free soils while the reverse was the case in the free oxides removed soils.

AMMONIUM ion when applied as salts of strong acids to soils is rapidly incorporated into the organic and inorganic fractions of the soils and are unavailable to plants. However, the immobilization or fixation of ammonium ions varies with the nature and characteristics of the soils. Per cent clay, nature of clay minerals, exchangeable potassium, amout of organic matter and cation exchange capacity[1-8] are the most important characteristics affecting the fixation or retention of applied ammonium ions. It has been well established that ammonium fixation in layer silicate minerals takes place by entrapment between adjacent aluminosilicate layers and consequent partial or total collapse of the mineral structure[1,4].

When a soluble phosphatic material is added to soil, it reacts with different components of soil and becomes relatively unavailable. Among the various components, iron and aluminium and their free oxides are most important[9-12]. A highly significant correlation has been established[13] between the amount of phosphate fixed and free iron oxide content in soils. Williams[14] also showed that when active aluminium was removed, the phosphate sorbing power was only about 10 per cent of the original soils, an observation also made by Chu and Sherman[15].

The free oxides of iron and aluminium may be present in films or as a surface coating on the clay particles, Therefore, removal of these oxides may modify the properties of the clay minerals. The present investigation has, therefore, been undertaken with a view to study the effect of organic matter and free iron and aluminium oxides on the fixation of ammonium and phosphate ions in some soils of West Bengal.

Experimental

Ten different soil samples of West Bengal were used for the present investigation. Two acid terai soils from Alipurduar and Phansidewa belonging to the northern district, two lateritic soils and one red soil from Bankura, Jhargram (Midnapur) and Purulia respectively, one coastal alluvium from Kakdwip (24 Parganas) and four other alluvial soils from Chakdah, Kalyani and Haringhata (Nadia) and Farakka (Murshidabad) were obtained as usual, air dried under shade, ground and sieved through a 0 2 mm sieve. The relevant characteristics of the soils are given in table 1.

The free oxides of iron and aluminium of a part of each soil were removed by the modified method of Mehra and Jackson[16]. The free oxide removed samples were then dried, ground and sieved through a 0.2 mm sieve.

Another part of each soil was treated with 6 per cent H_2O_2 to remove the organic matter.

Different soils were then incubated in tubes at 60 per cent moisture holding capacity of the soils at two different incubation periods and subjected to the following treatments. In one set phosphorus was added to the soil in the form of KH_2PO_4 at the rate of 100 ppm of P and in a second set $(NH_4)_2SO_4$ was added at the rate of 200 ppm of N.

Available phosphate of the soil samples were extracted by Olsen's method and the phosphate content was determined by the colorimetric procedure as described by Jackson[17]. The amount of NH_4-N fixed in 15 and 30 days was estimated by the recovery method developed by Bower[18] and Allison *et al*[19].

All estimations were done in duplicate and all the reagents and chemicals used in the present investigation were of A. R. quality.

TABLE 1 — PHYSICO-CHEMICAL CHARACTERISTICS OF THE SOILS

Soils	pH (1:2.5)	Organic carbon (%)	Clay (%)	c.e.c. me/100gm	Water holding capacity %	Free Fe_2O_3 %	Total P (ppm)	Native fixed NH_4^+ (ppm)
Alipurduar	5.4	1.600	28.0	8.9	50	0.87	500	176
Phansidewa	4.9	1.550	28.0	8.9	54	1.03	452	165
Bankura	5.6	0.600	20.0	10.2	35	1.82	276	140
Jhargram	5.1	0.435	30.0	7.5	32	2.46	252	149
Purulia	6.8	0.351	16.8	13.2	30	1.50	268	162
Kakdwip	6.0	0.825	70.0	29.2	62	1.66	515	340
Chakdah	6.6	0.800	26.0	31.7	60	1.90	410	326
Farakka	6.1	0.740	57.0	44.1	72	3.13	530	375
Haringhata	7.1	0.750	47.0	16.5	55	2.90	302	320
Kalyani	6.7	1.080	47.0	32.4	52	1.20	—	339

Results and Discussion

The amount of NH_4-N fixed in the soils in two incubation periods are given in table 2. It appears from the result that the fixation of NH_4-N bears a close relation with the clay content of the soils. Kakdwip soil containing higher amout of clay fixed a greater amount than the Bankura and Purulia soils containing comparatively lesser amount (Table 1). The results are in agreement with the findings of Bhaduri *et al*[9] who showed that the fixation of applied NH_4^+ bears a significant positive correlation with the clay content of some soils of West Bengal. Table 2 shows that with the increase of the incubation period the fixation does not increase so much indicating that ammonium fixation is a rapid process and maximum fixation (more than 90 per cent) occurs within 15 days.

The amount of NH_4^+ fixed by organic matter free soils is also given in table 2. As these soils are free from organic matter, the amount of NH_4^+ fixed depends solely on the amount of clay and the nature of the clay minerals. The results show that the amount of fixation is less than that of the original soils. This may be explained by the fact that hydrogen peroxide when added to the soils destroys the weakly as well as strongly bound native organic matter and in the course of the reaction the H_2O_2 molecule penetrates that lattices of the clays and thereby rupture them. As a result the dimension of the space between the two plates most probably increases and thereby the added NH_4^+ does not fix so much and can be easily leached out by 1(*N*)KCl solution. However, the decrease from the control in the fixation of NH_4^+ in the H_2O_2 treated soils is not so marked. With the increase of the incubation period the fixation in the H_2O_2 treated soils slightly increases. Gupta *et al*[10] obtained similar results in some soils of West Bengal.

The results on the fixation of applied NH_4^+ in the free oxide removed samples are also represented in table 2. It appears that there is a marked increase in the fixation of NH_4^+ over the control. The results clearly indicate that the presence of free oxides hinders the fixation of NH_4^+ by clay minerals by blocking the entrance of NH_4^+ ions between the clay plates. And this is possible if the free oxides form a coating or produce a film on the clay surface. The free oxides or hydrous oxides must have been bonding together surfaces made accessible to NH_4^+ after their removal. Farakka

TABLE 2—FIXATION OF NH_4-N(ppm) FROM THE ADDED $(NH_4)_2SO_4$

Soils	Original		Organic matter removed		Free oxide	
	15 days	30 days	15 days	30 days	15 days	30 days
Alipurduar	76.2	79.8	70.5	74.0	83.5	85.2
Phansidewa	70.2	76.2	64.0	66.2	78.2	88.0
Bankura	54.2	59.2	52.0	55.4	63.8	68.2
Jhargram	60.5	66.2	58.2	61.8	71.5	73.2
Purulia	58.6	60.0	56.0	59.8	66.2	66.8
Kakdwip	108.5	119.0	104.6	109.8	119.5	126.5
Farakka	99.2	109.2	96.0	101.4	114.2	122.4
Haringhata	98.0	106.3	96.4	99.8	109.2	118.4
Kalyani	96.0	104.1	95.0	99.8	109.0	113.8
Chakdah	60.2	66.2	55.4	59.0	71.2	79.3

soil containing higher amount of free iron oxides fixes a greater amount of NH_4-N after their removal.

The amount of added phosphate fixed in the soils are given in Table 3. The amount of added phosphate fixed is determined by subtracting the amount of phosphorus found in the available form from the amount added to the soil. It appears from the data that except in the case of acid soils of Alipurduar and Phansidewa the fixation of phosphate increases with the increase of the incubation period. The fixation of phosphate in the soils under present study may be due to chemical precipitation mainly by ferric and aluminium ions or their free hydrous oxide micelle. Table shows that the fixation of phosphate in the acid soils of Alipurduar and Phansidewa slightly decreases on prolonging the period of incubation. This may be explained by the fact that because of presence of higher amount of organic matter in these two soils microorganisms at the initial stage have multiplied rapidly and a part of the added phosphate has been used up to meet their nutritional requirement. On prolonging the period of incubation the amount of phosphorus fixed has been decreased because the phosphorus fixed in the organic form has gradually been mineralised and with the decomposition of organic matter many organic acids have been produced which solubilise the native fixed phosphorus.

TABLE 3 – FIXATION OF ADDED PHOSPHATE (PPM)

Soils	Original		Organic matter removed		Free oxide removed	
	15 days	30 days	15 days	30 days	15 days	30 days
Alipurduar	77.5	74.5	81.4	82.0	53.2	56.5
Phansidewa	74.5	70.0	79.2	83.0	53.4	56.0
Bankura	87.8	91.6	88.0	93.2	63.0	64.0
Jhargram	80.4	83.0	80.6	84.4	56.5	56.8
Purulia	80.6	84.0	80.8	86.0	55.8	56.4
Kakdwip	75.0	78.2	76.2	78.6	55.0	57.2
Chakdah	86.5	88.5	88.0	89.8	63.4	64.0
Farakka	89.6	94.5	90.8	95.5	48.6	48.6
Haringhata	83.5	86.2	84.2	86.4	50.3	50.0
Kalyani	79.5	84.5	80.5	85.6	53.4	54.0

Table 3 also reveals that except in the case of Alipurduar and Pnansidewa soils there is a marginal increase in the fixation of phosphate in organic matter free soils in 15 days but on prolonging the period of incubation the fixation also increases. Here also the fixation occurs due to the chemical precipitation mainly by ferric and aluminium ions or their free hydrous oxide micelle. The higher values of fixation of Alipurduar and Phansidewa soils may be due to the fact that the higher amount of organic matter present in these two soils forms complexes or chelates with Fe and Al. After the removal of organic matter the Fe and Al can easily react with phosphate producing insoluble precipitate.

The amount of added phosphate fixed by the free oxide removed soils at two incubation periods have also been given in table 3. The result shows that there is a considerable decrease in the fixation of phosphate in free oxide removed soils, the maximum decrease being located in the Farakka soil containing higher amount of free oxides. Except the soil of Haringhata all the soils are acidic in reaction (table 1). Fixation of phosphate in acid soils is mainly due to reaction of phosphate with iron and aluminium ions and their free oxides present in the soil. As the free oxides have imparted a great role in phosphate fixation in these soils, their removal has caused a great decrease in phosphate fixation capacity.

References

1. J. B. PAGE and L. D. BAVER, *Proc. Soil. Sci. Soc. Am.*, 1940, 4, 150.
2. J. I. WEAR and J. L. WHITE, *Soil. Sci.*, 1951, 71, 1.
3. F. E. ALLISON, E. M. ROLLER and J. H. DOETSCH, *Soil. Sci.*, 1953, 75, 173.
4. I. BARSHAD, *Soil. Sci.*, 1954, 77, 463.
5. W. D. BURGE and F. E. BROADBENT, *Proc. Soil Sci. Soc. Am.*, 1966, 30, 587.
6. W. C. HINMAN, *Canad. J. Soil Sci.*, 1966, 46, 223.
7. E. OPUWARIBO and C. T. I. ODU, *J. Soil Sci.*, 1975, 26, 350.
8. T. L. BHADURI, S. K. BANERJEE and S. K. GUPTA, *J. Indian Chem. Soc.*, 1977, 54, 822.
9. L. A. DEAN, *Adv. Agron.*, 1949, 1, 391.
10. C. K. RAJAGOPAL and M. A. IDNANI, *J. Indian Soc. Soil Sci.*, 1963, 11, 141.
11. J. S. KANWAR, *Soil Sci.*, 1956, 82, 43.
12. S. K. BANERJEE and B. DAS, *Technology*, 1977, 14, 49.
13. E. G. WILLIAMS, *Chem. and Ind.*, 1957, 47, 1533.
14. E. G. WILLIAMS, *J. Sci. Food Agric.*, 1958, 9, 551.
15. A. C. CHU and G. D. SHERMAN *Hawaii Agric. Exp. Sta. Tech. Bull*, 1952, 16.
16. O. P. MEHRA and M. L. JACKSON, *Clays and Clay Minerals*, 1958, 7, 317.
17. M. L. JACKSON, "Soil Chemical Analysis". Prentice-Hall, Inc., Engelwood Cliffs, N. J. 1958.
18. C. A. BOWER, *Soil Sci.*, 1950, 70, 375.
19. F. E. ALLISON, J. H. DOETSCH and E. M. ROLLER, *Soil Sci.*, 1951, 72, 187.
20. S. K. GUPTA, S. K. BANERJEE and A. K. MUKHERJEE, *J. Indian Chem. Soc.*, 1977, 54, 826.

J. Indian Chem. Soc.,
Vol. LVII, February 1980, pp. 191-194

Phenol Formaldehyde Cationic Matrices Substituted by Coal from Assam Mines

N. L. N. SARMA and PADMA VASUDEVAN*

Department of Chemistry, Indian Institute of Technology, New Delhi-110 029

Manuscript received 18 May 1979, revised 6 September 1979, accepted 31 December 1979

The sulfonated Assam Coal, which by itself acts as an exchanger was used to replace the polymeric matrix of phenol formaldehyde cation exchanger, varying the substituent content from 0 to 100%. All the important characteristics of the composites have been determined. It is observed that the substitution upto 30-40% is economical, since the composites obtained retain all the essential properties compared to the unsubstituted phenolic cationite.

SYNTHESIS and study of ion-exchangers is of interest because of their largescale use particularly in the softening of water. Since the current popular exchangers owe their origin to petroleum products, there is a continual increase in the cost of these exchangers.

There is a greater need now either to find out altogether newer resins which are economical compared to the existing exchangers or to identify substitutes which can partly replace the polymeric content of the existing exchangers to a considerable extent while the properties of the parent resin are retained. The impact of substitution will be more if the substituent itself acts as an exchanger. Earlier work done by the present authors revealed that coke[1], sawdust[2,3] and lignite[4] could be substituted upto 30-40% in phenolic cationites. The substitution did not have any adverse effect and in addition the composites obtained were macroporous[5].

The present work deals with the preparation and study of the properties of sulfonated phenolics, substituted partially by sulfonated coals obtained from Assam Coal Mines+.

Experimental

Materials and Reagents.

Coal from Assam Coal Mines; Phenol (BDH Reagent); Conc. sulfuric acid (Sp. Gr. 182); Formaldehyde (BDH Reagent).

(i) *Preparation of the samples :*

Phenol (300g) and sulfuric acid (365 ml) were mixed and heated to $\sim$100° on a water bath for two hours, cooled immediately in the ice and kept overnight. Assam coal samples of 25, 50, 75 and 100 g. were sulfonated with 50, 100, 150 and 200 ml of conc. sulfuric acid by heating on a water bath for four hours. The samples were mixed with 135 ml of phenol sulfonic acid so as to keep the percentage substitution of Assam coal respectively at 30, 45, 60 and 65. Each mixture was polymerised with 55 ml of 37% formaldehyde solution at 70°, ground, sieved and preserved for further work. These constitute the samples labelled AP I to AP IV. A separate sample of Assam coal was sulfonated and subjected to studies as such. The amounts of reagents used and the yields of samples are given in Table 1.

TABLE 1—AMOUNTS OF REAGENTS USED AND YIELDS OF THE COMPOSITES

Sample	Phenol Sulfonic acid, ml	Assam Coal g	Conc. H_2SO_4 ml	Formalin ml	Yield g	Assam coal in resin%
Unsubstitued resin	135	0	0	55	70	0
AP-I	135	25	50	55	110	20-25
AP-II	135	50	100	55	165	30
AP-III	135	75	150	55	180	40-45
AP-IV	135	100	200	55	240	40-45
Sulf. Assam Coal	0	100	100	0	120	10 0

*Senior Author, for correspondence.

+In revising this paper the referee has brought out that Assam coal could be treated with anthracene oil for a limited time period followed by sulfonation as done by the C.F.R.I.

(iii) *Physical Measurements* :

Swelling measurements were made by allowing the samples to equilibrate in water overnight. The wet weight was taken as M_w and the corresponding dry weight M_d was obtained after drying the same lot at 70° and then exposing to air. The gravimetric percent swelling, α, was measured from the equation

$$\alpha = \frac{M_w - M_d}{M_d} \times 100$$

Particle size was determined by sieving the samples in the sieves of 500, 300, 150 and 108μ.

Exchange capacity measurements were made by the method followed by Kunin[7]. The samples were converted into H^+-form by washing with HCl followed by distilled water to remove acidity. Known weight of wet samples in the H^+-form were equilibrated with standardised solutions of Na^+ (0.1M), Mg^{2+} (0.04M), and Ca^{2+}(0.04M). The following exchange occurred :

$$\text{Resin-}H^+ + M^+ \rightleftharpoons \text{Resin-}M^+ + H^+$$

where M^+ represents a metal ion.

The dry weight content of the samples equilibrated were determined by drying a part of the wet sample at 70° and weighing it. The exchange between H^+ in the resin and Na^+ in the solution was determined by titrating the supernatant against standard NaOH solution since there is an increase in the H^+ concentration of the supernatant due to the exchange. Exchange between Ca^{2+}/Mg^{2+} in the supernatunt and H^+ in the resin were determined by titrating against standard NaOH as well as EDTA. The latter measures the decrease in Ca^{2+}/Mg^{2+} concentration in the supernatant.

The total amount of Ca^{2+}/Mg^{2+} in the resin after exchange was separately estimated as follows., The known weight of the resin in Mg^{2+}-form was repeatedly washed with 100 ml of water till no trace of Mg^{2+} was there in the filtrate. The total Mg^{2+} thus extracted was estimated by EDTA titration. Subsequent to washing with water, the resin was eluted with 100 ml portions of HCl till no more Mg^{2+} was extracted. Once again in the filtrate, the amount of Mg^{2+} was estimated by EDTA tiration. The exchange capacity of big cations like $(NR_4)^+$ where R is methyl, ethyl or butyl was also determined as above from the pH change in the supernatant after equilibration with known amounts of the resin.

The surface areas of the samples were measured by PNP adsorption[8]. A standard solution of PNP in benzene (7g/lt) was prepared. 0.25-2 ml portions were dried and dissolved with several aliquots of water containing small amounts of NaOH. The absorbance of the solutions were measured at 400 nm. A calibration curve was thus prepared. For adsorption measurements, one gram of the dry resin was treated with 10 ml of PNP in benzene. The supernatant was treated as above and from the calibration curves the amount of PNP adsorbed was determined. The surface area was estimated from the PNP adsorbed, taking the PNP molecular occupancy to be 52.5Å^2.

Attrition stability of the samples of the composites were compared with that of unsubstituted resin as follows. Both types of sample were initially sieved to give batches containing particles greater than 500 μ in size. These were then swollen in water and shaken continously for six hours. Samples were separated by filtration, dried and weighed. Subsequently these were sieved on a 500 μ mesh size and amounts of the substance passing through the holes were weighed

Results and Discussion

The percent composition and physical characteristics of the exchangers are given in Table 1. The particle sizes are in the range of 500 μ-106 μ. The average percent swelling decreases from 100% resin to AP IV. Table 2 gives the data on attrition stability. As seen from columns 3 and 4 of Table 2, samples before shaking are made up of basically particles above 500 μ in size and less than 2-3% of the particles of small size. After shaking for 6 hours and repeating the sieving process

TABLE 2—ATTRITION EFFECT ON THE EXCHANGERS

Sample	Wt. of resin the taken, g	Before shaking			After shaking		
		Amount passed through 500 μ mesh g	%	Amount remained, g	Amount passed through 500 μ mesh g	%	Amount remained g
Unsubstituted resin	28.56	0.14	0.49	28.42	0.93	3.26	27.52
AP-I	19.29	0.08	0.41	19.21	0.41	2.1	18.88
AP-II	26.88	0.09	0.33	26.79	0.52	1.99	25.50
AP-III	20.95	0.33	1.57	20.62	0.39	1.93	19.80
AP-IV	27.88	0.21	0.75	27.68	0.30	1.09	27.05

it is observed that the percentage of particles less than 500μ in size formed due to attritional breaking during sieving is less than 2-3%. Also this is the same for the pure resin and the composites AP I to AP IV. Thus not much difference is seen in the attritional stability between the pure and the composite although in the latter it is possible that the resin might have formed in the capillaries of coal particles.

The apparent capacity for the exchange of Na^+ (0.1*M*) and Ca^{2+}/Mg^{2+} (0.04*M*) on the H^+-form of the exchangers and big cations NR_4^+ (0.04*M*) are listed in Table 3. As expected the exchange capacities are higher for the divalent ion as compared to Na^+ at the same concentration. Two interesting features may be noted. For any given ion, the capacity as determined by *p*H titration for AP-II containing 30% coal and AP-III containing 45% coal are comparable to that of pure resin. Sulfonated Assam coal itself has capacities of 0.6-0.8 meq/g. Fig. 1 is a plot of exchange capacity vs coal content in the resin. It is seen that though there is continuous decrease in capacity of coal the fall is not much up to 30-40%. This indicates that substitution of coal up to this extent is economical since the capacity of the composite is comparable with that of the unsubstituted resin.

Secondly, the capacities as determined by EDTA titrations for Ca^{2+}/Mg^{2+} are found to be higher than those obtained by *p*H titrations. This may be because the composite has considerable adsorption and binds some additional Ca^{2+}/Mg^{2+} by adsorption besides ion-exchange. While the *p*H titration will measure the hydrogen ions released by exchange, EDTA titrations give the total Ca^{2+}/Mg^{2+} which has been taken up by any method of binding including ion-exchange.

To check on the strength with which Ca^{2+}/Mg^{2+} ions are bound in the matrix, the resin was completely converted into Mg^{2+}-*form* and extracted with water subsequently. The results are shown in Table 4. As seen from the data, out of the total Mg^{2+} bound by the resin, some amount gets eluted by water itself indicating that the binding is loose and is probably held by adsorption. However, by HCl elution it is seen that the more

TABLE 3—CAPACITIES OF H^+-FORM OF THE COMPOSITES

Sample	Average swelling %	Exchange capacity in meq/g estimated by					
		Na^+ (0.1 *M*)	Mg^{2+} (0.04 *M*)		Ca^{2+} (0.04 *M*)		$(C_2H_5)_4N^+$ (0.04 *M*)
		*p*H	*p*H	EDTA	*p*H	EDTA	*p*H
Unsubstituted resin	200	1.82	1.78	1.78	1.78	1.78	—
AP-I	190	1.60	1.70	4.42	1.75	4.5	1.60
AP-II	135	1.58	1.6	4.00	1.65	2.6	1.55
AP-III	130	1.42	1.55	4.3	1.75	4.37	1.56
AP-IV	90	1.20	1.55	2.00	1.56	2.50	1.47
Sulf. Assam Coal	120	0.63	0.9	1.00	0.6	0.82	—

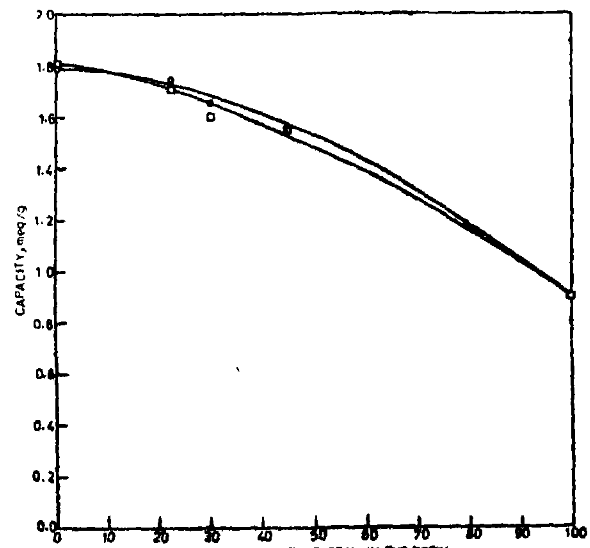


Fig. 1. Capacity VS percentage of coal in the exchanger. O [Ca^{2+}] = 0.04 *M*; □ [Mg^{2+}] = 0.04 *M*

TABLE 4—SORPTION/ION EXCHANGE PROPERTIES OF THE ION EXCHANGERS

Sample	Total amount of Mg^{2+} form of resin taken, g (dry weight)	Mg^{2+} eluted by water washing, meq.	Total Mg^{2+} eluted by subsequent HCL washing, meq.	Capacity, meq./g	
				Adsorbed Mg^{2+}	Exchanged Mg^{2+}
Substituted resin	2.73	1.58	4.60	0.56	1.68
AP-II	2.74	1.26	4.12	0.50	1.5
AP-III	3.17	2.21	7.54	0.70	2.37

strongly bound or exchanged Mg^{2+} is always greater than 1.5-1.8 meq/g. This is close to the value from *p*H titration. Thus, it seems that the composites can definitely bind up to 1.8 meq/g by exchange. Over and above this, there may be some additional adsorption. Further measurements on column capacity underway would determine the optimal useful capacity.

TABLE 5—SURFACE AREAS OF THE COMPOSITES.

Sample	Surface area, m^2/g
Unsubstituted resin	231
AP-I	100
AP-II	80
AP-III	96
AP-IV	60

In fact, the PNP-adsorption data (Table 5) indicate that the composites are porous. The surface area is of the order of 100 m^2/g. Thus, the samples combine ion-exchange capacity with adsorptive power. Also as shown in Table 2 the percent swelling in water is not high as compared to conventional gel type ion-exchangers indicating a certain rigidity in the matrix. Thus, these resins may prove useful where they are required to stand large osmotic shock. Since they have inherent porosity, the resins may be useful in non-aqueous solvents. As a result of porosity it is seen that even for the exchange of big ions of the type $(NR_4)^+$ the resins show their full capacity (cf. Table 2 last column) and are thus likely to be useful in the pharmaceutical industry.

Acknowledgement

The authors wish to thank M/s Ion Exchange (India) Ltd, Bombay and Council of Scientific and Industrial Research, New Delhi for financing the work.

References

1. N. L. N. SARMA, MARY JOSEPH and PADMA VASUDEVAN, *Res. Ind.*, New Delhi, 1976, **21**, 173.
2. PADMA VASUDEVAN and N. L. N. SARMA, *J. Appl. Polym. Sci.*, 1979, **23**, 1443.
3. PADMA VASUDEVAN and N. L. N. SARMA, Presented in the Symposium on Ion Exchange held at CSMCRI, Bhavnagar, India, 1978. 1.2 Book of Abstracts.
4. N. L. N. SARMA and PADMA VASUDEVAN, Lignite substituted phenolic cation exchangers (communicated).
5. PADMA VASUDEVAN *et. al.*, *J. Polym. Sci., Chem. Ed.*, 1978, **16**, 2545.
6. N. L. N. SARMA and PADMA VASUDEVAN, *J. Macromol. Sci. Chem.*, A, 1978, **12** (10), 1401.
7. R. KUNIN, Ion Exchange Resins, 3rd Edn. (John Wiley and Sons, New York) 1958, 338.
8. C. H. GILES and A. P. D'SILVA, *Trans. Faraday Soc.*, 1969, **65**. 1943.

J. Indian Chem. Soc.,
Vol. LVII, February 1980, pp. 195-196

The Catalysed Hydration of Nitriles to Amides

SISIR KUMAR ROY, SUBHASH CH. RAY and P. K. RAY

Central Fuel Research Institute, Dhanbad, Bihar.

Manuscript received 24 April 1978, revised 9 August 1979, accepted 31 December 1979

A simple, convenient and inexpensive process for the hydration of nitriles to amides under the influence of manganese-dioxide catalyst has been described. An aqueous solution of the nitrile is employed and the reaction is conducted at moderate temperature with reaction time of a few hours. In most instances nearly quantitative yields of amides are obtained with complete freedom from co-products or side reactions. The I. R. pattern of the catalysts are recorded with a view to correlating these properties with the catalytic activity. A plausible mechanism of the reaction is discussed.

THE hydration of nitriles to amides is catalysed by acids or alkalis in homogeneous phase and has been reported by several investigators[1,2]. The disadvantages inherent in the use of the alkalis or mineral acids are the formation of the corresponding organic carboxylic acids as by products with the corresponding decrease in the yield of the amides. Further, the product of such reaction would consist of a solution of a mixture of amide, the acid and the catalyst used which necessitates a rather elaborate separation step.

It appeared to us that by the use of water insoluble catalyst of either acidic/basic nature it should be possible to avoid or to minimise the hydrolytic action. With this concept various metals and metallic oxides, alkaline earth carbonates and alkali acid phosphates were tested.

Experimental

The procedure for hydration of pyridine 3-carbonitrile *to pyridine* 3-*carboxamide* (Nicotinamide) with manganese dioxide catalyst is shown as an example. The catalyst (1 gm) in 35 ml of water was placed in 250 ml round bottommed flask, and 5 gm of pyridine-3-carbonitrile (99.9% purity) was added. The flask was fitted with an Allihn condenser. The mixture was refluxed vigorously for about five hours. The catalyst was separated by filtration while hot and washed with hot water. The filtrate, admixed with washings, was evaporated on a waterbath. Nicotinamide was obtained as white crystals. The yield was 0.32–5.5 gm (with manganesedioxide catalyst prepared by different methods). The crude amide, although it was fairly pure, was recrystallised from hot water with a small quantity of active charcoal. Mpt. 129.5-130°. Identity was further confirmed by recording an IR spectrum and comparing it with that of an authentic specimen. Experimental conditions employed in different experiments are given in Tables.

Results and Discussion

The nitriles were hydrated to the corresponding amide by the catalytic action of metals like precipitated copper, nickel, metallic oxides like chromia, vanadia and manganesedioxide, alkaliphosphates and alkaline earth carbonates.

The yields of amides range from 20-95% of theory.

In a few cases, a small quantity of the corresponding acids is obtained by hydrolysis. However, nicotinamide itself is hardly over hydrolysed to nicotinic acid, even when it is refluxed for a long time with a newly prepared catalyst. In general, the hydration to an amide is predominant over other side reactions if the condition of the reaction is suitable. The features of this metal/metaloxide catalysed hydration are peculiar and unlike these of acid or base catalysed hydration.

Table 1 represents the comparative efficiencies of different catalyst system for the catalysed hydration of 3 & 4 pyridine-carbonitrile *to* pyridine carboxamide. *The highest yield of amide was obtained* with manganese dioxide catalyst followed by that with nickel.

Catalysed hydration with nickel as catalyst.

Table 2 represents the results of the experiments carried with nickel as hydration catalyst.

As a whole, electron attracting substituents give better yield of amide as is evident from the Table 2 Thus pyridine 3-&-4-Carbonitriles give a very high yield of amide, the nitrogen atom in the pyridine nucleus having an important electron attracting effect on the cyano group.

A remarkable ortho effect is also observed in this hydration reaction, which has been similarly recognised in the case of acid or alkaline hydration. The yield of amide is more or less diminished with ortho substituted benzonitrile such as ortho-tolunitrile. The reaction velocity becomes slower and often a considerable quantity of starting material is recovered unchanged.

TABLE 1—COMPARATIVE EFFICIENCY OF DIFFERENT CATALYSTS IN THE HYDRATION OF PYRIDINE CARBONITRILE TO PYRIDINE CARBOXAMIDES.

Catalyst	Wt. of Nitrile (gm)	Solvent c.c.	Reaction time (hr.)	Temp. 0°C	Yield of Amide (gm.)	Nitrile Recovered (gm.)
Na (OH)	Pyridine-4-Carbonitrile (5 gm)	50 c.c. N/2 soln.	5	100	5 gm.	Nil.
H_2SO_4	-do- (2 gm)	100 c.c. 90% H_2SO_4 soln.	5	100	1.2 gm.	0.3 gm.
$CaCO_3$ (2 gm)	Pyridine-3-Carbonitrile (5 gm.)	40 c.c. water	4	-do-	1.2 gm.	1.5 gm.
Na_2HPO_4 (2 gm.)	-do- (5 gm.)	40 c.c. water	5	-do-	3.6 gm.	0.8 gm.
$Li_3PO_4^-$ (2 gm)	-do- (5 gm.)	40 c.c. water	5	-do-	2.2 gm.	—
I.R.A. Amberlite 400	Pyridine-4-Carbonitrile (5 gm)	40 c.c. water	5	-do-	5 gm.	nil.
Activated Iron (2 gm)	Pyridine-4-Carbonitrile (10 gm)	35 c.c. water	5	-do-	2 gm.	5.2 gm.
V_2O_5 (1 gm)	Pyridine-4-Carbonitrile (10 gm)	35 c.c. water	5	-do-	1 gm.	6.3 gm.
MnO_2 (1 gm)	Pyridine-3-Carbonitrile (5 gm)	35 c.c. water	5	-do-	5.37 gm.	—
Cr_2O_3 (1 gm)	Pyridine-3-Carbonitrile (4 gm)	35 c.c. water	5	-do-	1.3 gm.	0.9 gm.
Ni (1 gm)	Pyridine-3-Carbonitrile (7 gm)	100 c.c. water	10	-do-	5.2 gm.	—
PPted Cu (1 gm.)	Pyridine-4-Carbonitrile (5 gm)	35 c.c. water	5	-do-	1.07 gm.	—

The purity of Pyridine 3 and 4-Carbonitriles (E Merck) used is 99.9%.

TABLE 2—THE HYDRATION OF NITRILE TO AMIDE WITH NICKEL 5 gm. OF NICKEL USED IN EACH CASE.

Temperature 100°C.

Compound	Water c.c.	Reaction time. hr.	Yield of amide (wt. %)
Benzonitrile (E Merck) (5 gm)	80	10	60
o-Tolunitrile (E Merck) (5.5 gm.)	80	12	32
Pyridine-3-Carbonitrile (7 gm)	100	10	70
Pyridine-4-Carbonitrile (5 gm)	100	10	73

Catalysed hydration with manganesedioxide as catalyst

From Table 1 it is observed that of all the catalysts, manganese dioxide exhibited highest selectivity and activity towards hydration of nitriles to amides. Therefore, investigation on different aspects of hydration reaction, so as to optimise the yield of nicotinamide has been carried out with this catalyst.

Effect of methods of preparation of the catalyst :

Table 3 represents the results of the experiments carried out under comparable conditions with manganese dioxide prepared by different methods. It was found

TABLE 3—COMPARATIVE EFFICIENCY OF MANGANESE DIOXIDE CATALYSTS PREPARED BY DIFFERENT METHODS. 1 gm OF MnO_2 AND 5 gm. OF PYRIDINE-3-CARBONITRILE USED IN EACH CASE, WATER USED 35 CC, REACTION TIME 5 (FIVE) HOURS, TEMPERATURE 100°C.

Catalyst MnO_2, 1 gm.	Yield of Amide gm.	Nitrile recovered gm
F.	5.5	Nil
E.	5.75	1.08
H.	0.32	2.07
I.	5.7	nil.

F. (MnO_2 from Mn-acetate + H_2SO_4 + $K_2S_2O_8$).
E. (MnO_2 from $MnCl_2.4H_2O$ + $KMnO_4$).
H. (MnO_2 from $Mn(NO_3)_2$ xH_2O heated upto 400°C).
I. (MnO_2 from $MnSO_4$ + $KMnO_4$).

that two particular methods of preparation* of the catalyst result in the highest selectivity of the catalyst for hydration of pyridine carbonitriles to amides.

Reaction temperature :

The operating temperature is specific to the catalyst and the upper limit to the temperature is determined by the onset of over hydrolysis giving rise to undesirable side products like acids. The lower limit is set by the rate of reaction that can be economic. The temperature range of 60-100° has been investigated with reference to these considerations. It is observed from Table 4 that with increase in temperature, the yield of amide increases and reaches maximum at 100°.

TABLE 4—EFFECT OF TEMPERATURE ON THE CONVERSION OF NITRILE TO AMIDE.

Catalyst Manganese dioxide 1 gm. Water 35 c.c., Pyridine-3-carbonitrile (5 g.)

No. of obs.	Temp. °C	Nicotinamide (pyridine-3-carboxamide) (Wt. %)
1.	62	48
2.	85	67
3.	90	100
4.	100	114

Reaction time :

Low reaction time favours incomplete hydrolysis, while a high reaction time results in an excess of over-hydrolytic product like acids. It is evident from Table 5 that a reaction time of 5 hrs, is optimum for the catalytic hydration of pyridine 3-carbonitrile to Nicotinamide.

TABLE 5—EFFECT OF REACTION TIME ON THE CONVERSION OF NITRILE TO AMIDE.

Solvent : 35 cc water, Nitrile : Pyridine-3-carbonitrile 5 gm., Catalyst manganese dioxide 1 gm.

No. of obs.	Reaction Time, hr.	Yield of Amide (wt. %)
1.	2.5 hr	40
2.	4	79
3.	5	108
4.	8	85

Catalyst/substrate ratio :

Table 6 represents the result of the experiments carried out with different ratios of weight of the catalyst (in gms) to the moles of feed. It is observed that the yield of nicotinamide from pyridine 3 carbonitrile is not appreciably affected in the range 0.025 to 0.1.

TABLE 6—EFFECT OF THE W/F, ON THE CONVERSION OF NITRILE TO AMIDE.

Solvent-water 35 cc. Catalyst manganese dioxide, Nitrile (5 g.) Pyridine-3-carbonitrile, Temp. 100°C, reaction time 5 hrs.

No. of obs.	W/F.	Yield of Amide (wt. %)
1.	0.1018	87.5
2.	0.1006	96.24
3.	0.0502	93.7
4.	0.0250	87.5

Mechanism of action of Nickel :

When ortho-nitro benzonitrile was hydrogenated either in the liquid or vapour phase[3], it was reported that a considerable quantity of orthoaminobenzamide was formed by the hydration of nitrile group. It has been presumed[4] that the hydrogenating activity of the nickel catalyst is largely depressed by poisoning with amine group produced by the reduction of nitrogroup and that the nitrile group is hydrated with the water produced by the hydrogenolysis of nitro group originally present in the system. The present investigation shows that such is the case since the ability of the nickel catalyst to effect the hydration of nitrile group has been proved.

It is noteworthy that nitrile group, of basic character such as Pyridine 3-carbonitrile and Pyridine-4-carbonitrile give good yields of amide, whereas those of acidic character such as *p*-hydroxy benzonitrile gives no hydration product.

According to the studies of reaction mechanism of the hydrolysis of nitriles with acid or alkali[7], the hydration has been assumed to be initiated at the carbon atom of the nitrile group, endowed with a carbonium ion character. In the catalytic hydration of nitriles, the reaction may be similarly initiated at the carbon atom attached to the basic sites of the catalyst.

Mechanism of action of manganese dioxide catalyst :

The role of manganese-dioxide in the reaction has not yet been elucidated. It may be postulated that since the reaction is biphasic, adsorption of the substrate is followed by hydrolysis and subsequent desorption of the product. The more easily hydrolysable compounds, are however, those that would be expected to form the most stable carbonium ion[6], which may perhaps play an important role in the reaction mechanism.

*(1) Reduction of Potassium permanganate with manganous salts.
(2) Reaction of Manganese acetate with potassium persulphate.

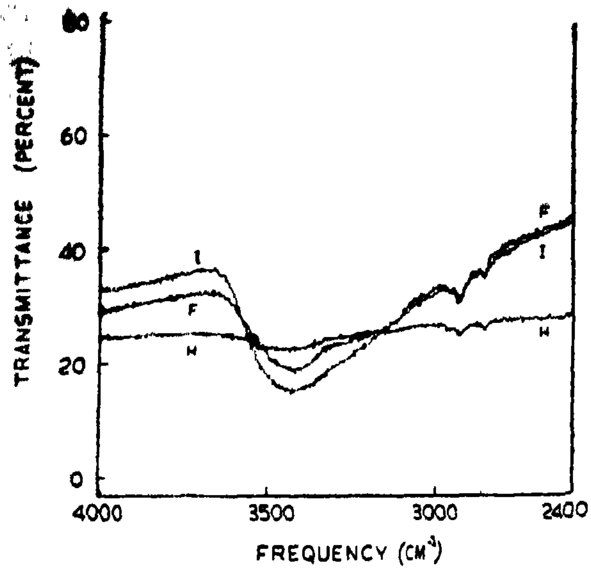


Fig. 1. I.R. Spectra of variously prepared MnO_2 samples in the region 2400 cm^{-1} – 4000 cm^{-1}.

I —I.R. Spectrum of MnO_2
F—I.R. Spectrum of MnO_2
H—I.R. Spectrum of MnO_2

The peculiar effectiveness of manganese dioxide may in part be related to the fact that as ordinarily prepared by precipitation it is a "non stoichiometric" compound, has oxygen content slightly less than that corresponding to the dioxide[6], and also contains water (3-4%) which can not be removed thermally without some further loss of oxygen. The water is probably present as hydroxyl group linked to manganese. To confirm this statement I. R. of different samples of MnO_2 prepared by different methods were recorded and in some cases broad bands in the region 3100-3600 cm^{-1} were observed (Fig. 1) indicative of the presence of -O-H groups. The formation of hydroxylated intermediate may be assisted, if not caused, by these hydroxyl groups in the dioxide resulting in the formation of amides.

Acknowledgement

The authors gratefully acknowledge the help and encouragement received from Dr. M. G. Krishna, Director (Ex), Central Fuel Research Institute. The anthors also thank Mr. G. S. Murty for rendering considerable help in analysis.

References

1. C. F. Krewson and J. F. Cench, *J. Amer. Chem. Soc.*, 1943, 65, 2256.
2. British patent 563, 184 (1944).
3. H. Rupe, *Helv. Chim. Acta.*, 1925, 8, 832.
4. K. Watanabe, *J. Chem. Soc. Japan, Pure Chem.* Section. 1955, 76, 398 ; *Chem. Abs.*, 1957, 51, 17815.
5. "The Chemistry of Cyano group" ZVI RAPPOPORT, Interscience publishers, 1970, p. 259.
6. J. T. Grey, *J. Amer. Chem. Soc.*, 1946, 68, 605.
7. "The Chemistry of Cyano group" ZVI RAPPOPORT, Interscience publishers, 1970, p. 256.

J. Indian Chem. Soc.,
Vol. LVII, February 1980, pp. 199-202

Studies with Model Membranes : Evaluation of the Thermodynamically Effective Fixed Charge Density and Test of the Theories of Membrane Potential and Bi-ionic Potential Based on Thermodynamics of Irreversible Processes

M. NASIM BEG*, FASIH A. SIDDIQI**, BADRUL ISLAM and AKMAL HUSAIN

Physical Chemistry Division, Department of Chemistry, Aligarh Muslim University, Aligarh-202 001 (India).

Manuscript received 13 June 1978, revised 30 July 1979, accepted 31 December 1979

Membrane potentials and bi-ionic potentials across two parchment supported Cobalt and Chromium orthovanadate membranes using various 1:1 electrolytes have been reported. Theoretical equations based on thermodynamics of irreversible processes for membrane potentials and bi-ionic potentials, derived recently by Nagasawa *et al* and Toyoshima and Nozaki have been applied to derive the thermodynamically effective fixed charge density which is an important parameter governing the membrane phenomena and other membrane parameters. The derived membrane parameters have been used to predict bi-ionic potentials across the membranes. Theoretical predictions were borne out quite satisfactorily by our experimental results.

THERMODYNAMICALLY effective fixed charge density which is an important parameter governing the membrane phenomena has been one of the most widely characterized electrochemical and bio-electric phenomena. Based on the fixed charge concept[1,2] a number of mathematically rigorous equations for membrane potential have in recent years, been derived[3-6] and their validity examined by taking model membrane systems[7-15]. Most recently Nagasawa and coworkers[16-17] as well as Toyoshima and Nozaki[18] have derived equations for membrane potential utilizing the principles of non-equilibrium thermodynamics[6]. In this paper we describe a series of electric potentials observed across cobalt and chromium orthovanadate membranes separating various 1:1 electrolytes at different concentrations for the evaluation of effective fixed charge density of the membranes utilizing the recently developed equations for membrane potential. An effort has been made to examine the validity of the equations developed.

Experimental

Preparation of Membranes :

Cobalt and Chromium orthovanadate membranes were prepared by the method of interaction suggested by Siddiqi Beg and coworkers[7-15].

The electrochemical cell of the type

Reference electrode	Solution C_1	Membrane	Solution C_2	reference electrode

was used for measuring electrical potentials arising across the membrane by maintaining a ten fold difference in concentration (i.e. $C_2/C_1=10$) and using a Pye Precision Vernier Potentiometer (No. 7568). The bi-ionic potentials were determined by taking two electrolytes of the type AP and BP of the same concentration in place of the solutions C_1 and C_2. The salt solutions (Chloride of K^+, Na^+ and NH_4^+) were prepared from analytical grade reagent (B.D.H.) using deionized water.

Results and Discussion

When two electrolyte solutions of different concentrations are separated by a membrane, mobile species penetrate the membrane and various transport phenomena are induced in the system. The fixed charge concept of Teorell-Meyer-Sievers is the pertinent starting point for investigation of actual mechanisms of transport of molecular or ionic processes in the membrane phase. The theory has been generally accepted and widely used for the evaluation of membrane parameters using potentiometric method. Recently Nagasawa *et al*[16,17], based on the theory of irreversible processes, have derived equation for membrane potential. The total membrane potential $\Delta\phi_m$ was considered as the sum of diffusion potential $\Delta\phi_d$ inside the membrane and the electrostatic potential difference $\Delta\phi_e$ between the membrane surfaces and electrolyte solutions on both sides of the membrane. These authors derived the

**Present address : Dr. Fasih A. Siddiqi, Department of Biophysics, Michigan State University, East Lansing, Michigan 48824 (U.S.A.).

following equation for membrane potential

$$-\Delta\phi_m=\frac{RT}{F}\left(\frac{\bar{X}}{2}\right)\left(\frac{\sigma-1}{\sigma}\right)\frac{1}{C'}+\frac{RT}{F}\frac{U_+-U_-}{U_++U_-}$$

$$\times\left[\frac{1-\dfrac{XJ_0}{RTC_0(U_+-U_-)k}}{1-\dfrac{XJ_0}{2RTC_0U_+K}}\right]\ln\sigma$$

$$+\frac{RT}{2F}\frac{X}{U_+U_-}\frac{J_0}{RTC_0K}\frac{\left[1-\dfrac{XJ_0(U_++U_-)}{4RTC_0U_+U_-K}\right]}{\left[1-\dfrac{XJ_0}{2RTCU_-K}\right]^2}(\sigma-1)C' \qquad (1)$$

At sufficiently high electrolyte concentrations eq. (1) was approximated to

$$\Delta\phi_m=\frac{RT}{F}(\sigma-1/\sigma)(\bar{X}/2)/C'+\ldots \qquad (2)$$

This equation predicts a linear relationship between membrane potential $\Delta\phi_m$ and $1/C'$. The values of $\Delta\phi_m$ [Table 1] were plotted against $1/C'$. A set of straight lines in Figs. 1 and 2 point towards the correctness of the theory. The values of $\bar{X}$ were calculated from the slope of the lines and are given in Table 2. The values are quite low which is in agreement with our earlier findings of diffusion rate studies.

TABLE 1—MEMBRANE POTENTIALS mV OBTAINED THROUGH CHROMIUM AND COBALT ORTHOVANADATE MEMBRANES

Concentrations (eq/l)	Chromium orthovanadate KCl	NaCl	NH_4Cl	Cobalt orthovanadate KCl	NaCl	NH_4Cl
1/0.1	7.85	−5.05	3.06	15.55	0.60	3.80
0.5/0.05	13.52	−1.82	7.22	22.34	3.15	8.00
0.1/0.01	18 70	18.45	23.65	26.75	20.80	25.72
0.05/0.005	24.10	28.05	30.25	29.20	27.82	31.35
0.01/0.001	29.35	32.85	34.45	32.50	31.40	35.00
0.005/0.0005	31.05	34.05	35.10	34.00	32.95	34.45
0.001/0.0001	32.25	34.35	35.29	35.55	34.15	35.95

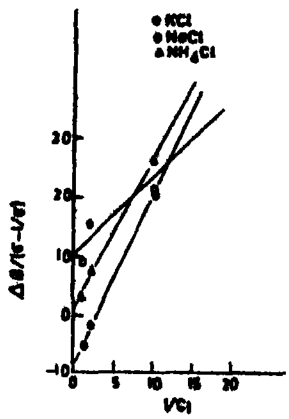


Fig. 1. Plots of $\Delta\phi_m(\sigma-1)/\sigma$ vs $1/C'$ for various electrolytes with Chromium orthovanadate membrane.

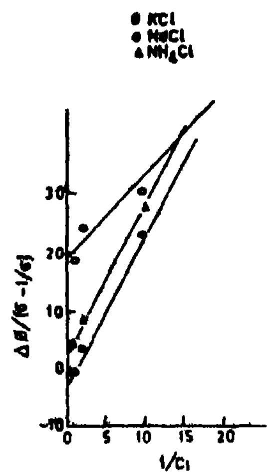


Fig. 2. Plots of $\phi_m/(\sigma-1)/\sigma$ vs $1/C'$ for various electrolytes with Cobalt orthovanadate membrane.

TABLE 2 – DERIVED VALUES OF THE MOBILITY RATIO (U_+/U_-), CHARGE DENSITY ($\bar{X}$) OF CHROMIUM AND COBALT ORTHOVANADATE BY TMS AND NAGASAWA METHOD.

Electrolytes	Chromium orthovanadate TMS Method U_+/U_-	Chromium TMS Method Xeq/lit	Chromium Nagasawa Method Xeq/lit	Cobalt orthovanadate TMS Method U_+/U_-	Cobalt TMS Method Xeq/lit	Cobalt Nagasawa Method Xeq/lit
KCl	1.20	1.778×10^{-3}	1.784×10^{-3}	1.00	6.309×10^{-3}	1.779×10^{-3}
NaCl	0.80	2.511×10^{-3}	3.662×10^{-3}	0.80	3.981×10^{-3}	3.192×10^{-3}
NH_4Cl	1 00	2.818×10^{-3}	3.202×10^{-3}	1.00	3.548×10^{-3}	3.202×10^{-3}

Most recently Toyoshima and Nozaki[10] derived theoretical equations for membrane potential and bi-ionic potential using certain crucial assumptions for mobility and activity coefficients of ions within the membrane. The theoretical equation for BIP was

$$\Delta\phi_{BIP}=2\ln(K_A/K_B)+\ln(JV_A+1)/(JV_B+1)\left(\frac{F}{RT}\right) \quad (3)$$

where the symbol K_A/K_B is called the selectivity constant for + ion species. The flux J and the membrane

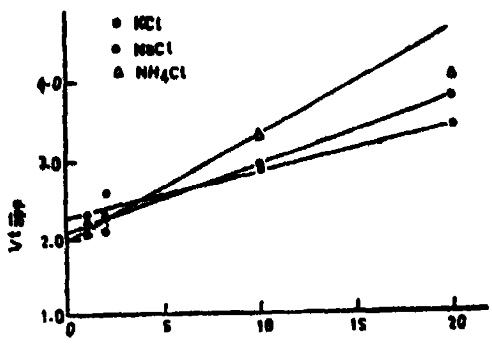


Fig. 3. Plots of $1/t^-_{app}$ vs 1/C for Chromium orthovanadate membrane.

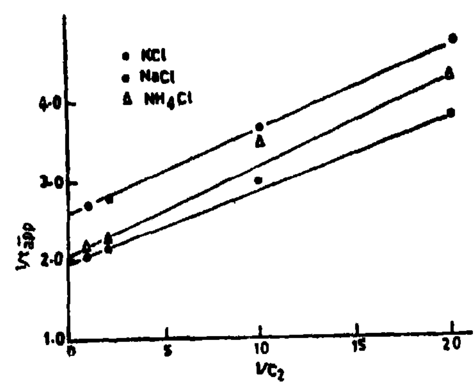


Fig. 4. Plots of $1/t^-_{app}$ vs 1/C for Cobalt orthovanadate membrane.

parameters V_N and $\bar{X}/K_N$ were expressed as follows

$$V_N=1+U^0_N/U^0_P \; (N=A,\ B) \quad (4)$$

$$(2J+1)\ln(gA+2J)/(gB+2J)\ -\ \ln(JV_A+1)/(JV_B+1)$$
$$-\ln(gA/gB)=0 \quad (5)$$

and

$$gN=1+\sqrt{1+(2K_N\,C/X)^2} \quad (6)$$

In order to derive the values of V_N and $\bar{X}/K_N$, Toyoshima and Nozaki have derived another expression (eq. 7).

$$\frac{1}{t_-}=V_N+(V_N-1)(\sigma-1)/\sigma\ln\sigma(\bar{X}/K_N)(1/C_N)+\ldots \quad (7)$$

When the transference number t_- was defined by the Nernst eqn.

$$\Delta\phi=\frac{RT}{F}(1-2t_-)\ln\sigma \quad (8)$$

The values of V_N and $\bar{X}/K_N$ were obtained from the intercept and slope of the linear plots of $\frac{1}{t_-}$ vs $\frac{1}{C_N}$. The

TABLE 3—DERIVED VALUES OF PARAMATERS $\bar{X}/K_N$, V_N OF CHROMIUM AND COBALT ORTHOVANADATE MEMBRANE USING VARIOUS ELECTROLYTES.

Membranes	Electrolytes	Parameters $\bar{X}/K_N$	V_N
Chromium orthovanadate	KCl	0.28	2.28
	NaCl	0.34	2.07
	NH_4Cl	0.53	2.00
Cobalt orthovanadate	KCl	0.38	2.58
	NaCl	0.36	1.95
	NH_4Cl	0.45	2.05

TABLE 4—DERIVED VALUES OF g_N (N = KCl, NaCl, NH_4Cl) ACROSS CHROMIUM AND COBALT ORTHOVANADATE MEMBRANES.

Membrane	Chromium orthovanadate			Cobalt orthovanadate		
Concentration (eq/lit)	g_{k^+}	g_{Na^+}	$g_{NH_4^+}$	g_{k^+}	g_{Na^+}	$g_{NH_4^+}$
0.5	4.709	4.107	3.135	3.820	3.952	3.437
0.1	2.229	2.160	2.069	2.130	2.144	2.094
0.05	2.062	2.042	2.018	2.034	2.038	2.024
0.01	2.003	2.002	2.001	2.001	2.002	2.001
0.005	2.000	2.000	2.000	2.000	2.000	2.000
0.001	2.000	2.000	2.000	2.000	2.000	2.000

values of V_N and $\bar{X}/K_N$ thus derived were then used in eq (6) to get the values for gN. Finally the value of the flux J was calculated using eq (5). Once

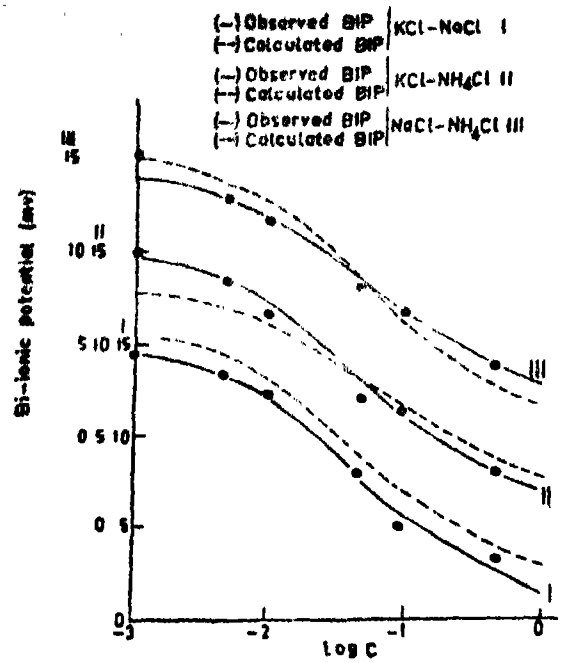


Fig. 5. Plots of observed (— — —) and calculated (- - - - - -) bi-ionic potentials $\Delta\phi$ vs log C for different pairs of electrolytes with Chromium orthovanadate membrane.

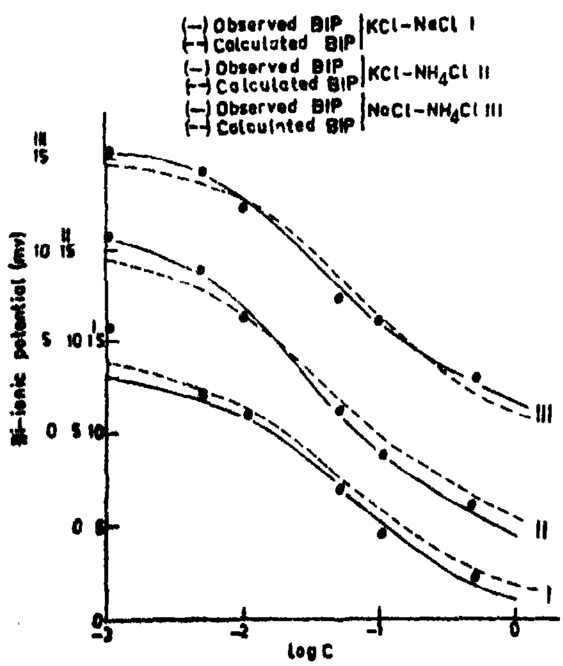


Fig. 6. Plots of observed (———) and calculated (- - - - - -) bi-ionic potentials $\Delta\phi$ vs log C for different pairs of electrolytes with Cobalt orthovanadate membrane.

the membrane parameters J, V_N, $\bar{X}/K_N$, gN are known, one can calculate theoretical bi-ionic potential using eq.(3). The theoretical bi-ionic potentials thus calculated were plotted as a function of C_s in Figs. 5 and 6. The observed bi-ionic potentials were also plotted in the same graphs. Figs. 5 and 6 demonstrate that the theoretical predictions are borne out quite satisfactorily by our experimental results. However, a little deviation may be due to various reasons most notably due to the different degree of ionic interactions with the membrane skeleton at different electrolyte concentrations.

Acknowledgement

The authors are grateful to Prof. W. Rahman, Head, Department of Chemistry, Aligarh Muslim University. Aligarh for providing the necessary research facilities and also to C.S.I.R. (India) for the award of fellowships to Badrul Islam and Akmal Husain.

References

1. T. Teorell, *Proc. Soc. Expt. Med. Biol.*, 1935, 33, 282; *Proc. Natl. Acad. Sci.* (*U. S.*), 1935, 21, 152; *Z. Elektrochem.*, 1951, 55, 460; *Progr. Biophys. Chem.*, 1953, 3, 305.
2. K. H. Meyer and J. Sievers, *Helv. Chim. Acta.*, 1936, 19, 649, 665, 987.
3. Y. Kobatake, T. Noriaki, Y. Toyoshima and H. Fujita, *J. Phys. Chem.*, 1965, 69, 3981.
4. Y. Toyoshima, M. Yuassa, Y. Kobatake and H. Fujita, *Trans. Faraday Soc.*, 1967, 63, 2803, 2814; *J. Phys. Chem.*, 1968, 72, 2871.
5. N. Kamo, Y. Toyoshima, H. Nozaki and Y. Kobatake, *Kolloid-Z. Z. Polymer*, 1971, 249, 1061; *Kolloid-Z Z. Polymer*, 1971, 248, 914.
6. N. Kamo, M. Ockawa and Y. Kobatake, *J. Phys. Chem.*, 1973, 77, 2995.
7. F. A. Siddiqi, M. N. Beg and P. Prakash, *J. Electroanal. Chem.*, 1977, 80, 233.
8. M. N. Beg, F. A. Siddiqi and R. Shyam, *Canad. J. Chem.*, 1977, 55, 1680.
9. F. A. Siddiqi, M. N. Beg, M. Ibadur Rahman Khan, S. K. Saksena, A. Haque and Badrul Islam, *Canad. J. Chem.*, 1978, 56, 2205.
10. F. A. Siddiqi, M. N. Beg and S. P. Singh, *J. Polym. Sci.*, 1977, 15, 959.
11. M. N. Beg, F. A. Siddiqi, R. Shyam and I. Altaf, *J. Electroanal. Chem.*, 1978, 89, 141.
12. M. N. Beg, F. A. Siddiqi, Akmal Hussain and Badrul Islam, Lipids (in press).
13. F. A. Siddiqi, S. K. Saksena, M. I. R. Khan and M. A. Ahsan, *J. Memb. Sci.*, 1977, 2, 245.
14. F. A. Siddiqi, M. N. Beg, Ibadur Rahman Khan, M. A. Ahsan and Badrul Islam, *J. Memb. Sci.*, 1978, 4, 275.
15. F. A. Siddiqi, M. N. Beg, A. Haque, M. A. Ahsan and M. I. R. Khan, *J. De Chimie Physt.*, 1977, 74, 932.
16. M. Nagasawa and I. Kagawa, *Discuss. Faraday Soc.*, 1956, 21, 52.
17. M. Tasaka, N. Aoki, Y. Konda and M. Nagasawa, *J. Phys. Chem.*, 1975, 79, 1307.
18. Y. Toyoshima and H. Nozaki, *J. Phys. Chem.*, 1970, 74, 2704.

J. Indian Chem. Soc.,
Vol. LVII, February 1980, pp. 203-207

On the Characterization of Membranes

KEHAR SINGH,* RAJ KUMAR ** and V. N. SRIVASTAVA***

Chemistry Department, Gorakhpur University, Gorakhpur-273 001, India

Manuscript received 8 February 1979, revised 12 September 1979, accepted 31 December 1979

Characterization of membranes on the basis of conductance and permeability data has been discussed. Membrane constant and equivalent pore radius of a Pyrex-G_4 membrane equilibrated with sodium chloride, potassium chloride, barium chloride and aluminium chloride solutions have been estimated. These membrane parameters and zeta-potentials have also been determined in the case of Zeokarb-225 (H^+ form) membrane using methanol-water mixtures as permeants. Characterization of an aluminium-oxide membrane has also been accomplished from permeation data obtained at different temperatures.

NON-equilibrium thermodynamic treatment[1-4] is often used for the description of membrane transport phenomena occuring under the simultaneous action of gradients of hydrodynamic pressure and electrical field. This treatment is independent of structural details of the membrane and characterises the system in terms of a set of experimentally accessible phenomenological coefficients. For a proper understanding and prediction of a membrane permeation characteristics, however, an insight into the structural details, e.g., effective cross-sectional area, equivalent pore radius and the electrical character of the membrane permeant interface are needed.

In the present communication, we report studies on hydrodynamic and electroosmotic permeabilities of water and aqueous electrolyte solutions through a pyrex membrane. Similar measurements with (i) zeokarb-225 (H^+ form), ion-exchange membranes, using methanol and methanol-water mixtures as permeants and (ii) an aluminiumoxide membrane using methanol as permeant at different temperatures, have also been carried out. Electrical conductivities of the equilibrated membranes have also been measured. The data have been used to ascertain membrane permeation characteristics.

Experimental

Zeokarb-225 (Na^+ form), obtained from Permutit Company London, was used for the preparation of the ion-exchange membranes. It had an exchange capacity of 4.8 meq/gm dry resin and moisture content equal to 50% by weight.

It was converted into H^+ form by equilibrating it with 1 molar HCl for over 24 hours. The particles were then repeatedly washed with distilled water in order to remove the excess acid present. Ion-exchange membranes was then prepared by the mechanical compression as described earlier[1,2,5]. Pyrex-G_4 sinter was also used as a membrane. It was cleaned in the usual manner[6]. Aluminium oxide membrane was prepared by taking a small amount of basic active aluminium oxide (B.D.H.) along with a small amount of an adhesive, Araldite, and keeping it compressed mechanically in the middle of a glass tube for over 24 hours. The plug formed was 1.6 cm long and 1.2 cm in diameter. Sodium chloride, potassium chloride, barium chloride, aluminium chloride and methanol (AR, BDH) was used without further purification. Distilled water was double distilled with alkaline $KMnO_4$. Specific conductivity of the water used was of the order of 1^{-6}mhos- cm^{-1}.

Hydrodynamic and electroosmotic permeabilities were measured by using the experimental procedure described in our earlier publications[1,2,5]. An electronically operated power supply was used for the application of electrical potential difference. The rate of permeation was estimated by noting the movement of the permeant in a horizontally placed graduated capillary tube of known cross-sectional area. Conductance of the membrane and specific conductivity of the permeant were measured by means of a conductivity bridge at 50 cycles/sec. Viscosities of the methanol-water mixtures were measured with a modified Tuonfuoss viscometer[7]. The measurements were carried out in an air-thermostat maintained at 303 ± 3.5 K, in the case of pyrex and zeokarb-225 membranes and at 298, 303, 308, 313 ± 0.5 K, in the case of aluminium oxide membrane.

Results and Discussion

The rate of permeation through a membrane under the action of hydrostatic pressure and/or electrical

* Visiting Scientist, Membrane Research Division, The Weizmann Institute of Science, Rehovot, Israel.

** Physical Chemist, Chemistry Division, Ahmedabad Textile Industries Research Association (ATIRA), Ahmedabad-380 015.

***Teacher Research Fellow, from K. S. Saket Post-graduate College, Ayodhya, Faizabad (U.P.) 224 001.

gradient depends on the effective cross-sectional area, A, and the thickness of the membrane, l. An unambiguous determination of either of these quantities is difficult due to complex geometry of the openings within the membrane. It is, however, possible to determine A/l, the membrane constant, in terms of which permeation behaviour of any membrane can be quantitatively expressed.

Let us consider a membrane having n pores of equivalent radius 'r' and effective length, l. The effective cross-sectional area, A, of this membrane through which permeation occurs is $n\pi r^2$. The electrical conductance of the membrane equilibrated with a permeant having specific conductivity, k, is given by[8]

$$K = \frac{n\,\pi\,r^2\,k}{l} = \frac{A}{l}\,k \quad \cdots (1)$$

so that, the membrane constant ; $\frac{A}{l} = \frac{K}{k}$ ... (2)

The membrane conductance can thus easily be used for the determination of membrane constant. This constant is characteristic of the membrane and is independent of the nature of the permeating liquid, so long as interaction between the permeant and the membrane matrix is not strong enough to alter its equivalent pore radius. Membrane constant values obtained from conductance data are given in Tables 1, 2, 3 and 4 for different membrane permeant systems.

TABLE 1—MEMBRANE CHARACTERISTICS FOR PYREX/ELECTROLYTE SYSTEM : AT 303 ± 0.5 K.

Electrolyte/ Concentration (Moles litre^{-1})	$L_{11} \times 10^5$ (cm^{5}sec^{-1} dyne^{-1}K)	$L_{12} \times 10^8$ (cm^{3}sec^{-1} volt^{-1}K)	$K \times 10^6$ (Mhos)	$k \times 10^5$ (Mhos-cm^{-1})	$\frac{A}{l} \times 10^1$ (cm.)	$r \times 10^4$ (cm.)
NaCl						
0.0000	9.88	4.48	1.50	1.19	1.25	4.07
0.0001	9.39	5.24	2.60	2.55	1.02	4.41
0.0005	9.64	7.24	7.50	6.52	1.15	4.21
0.0010	9.51	8.18	12.00	11.22	1.07	4.33
KCl						
0.0000	8.94	4.82	1.30	1.19	1.09	4.16
0.0001	9.03	5.58	2.50	2.13	1.12	4.03
0.0005	9.70	6.33	8.00	6.82	1.17	4.18
0.0010	9.27	6.61	15.00	—	—	—
$BaCl_2$						
0.0000	13.15	3.82	1.50	1.08	1.39	4.47
0.0001	13.33	4.48	3.50	2.43	1.44	4.42
0.0005	13.18	5.21	14.00	10.08	1.39	4.48
0.0010	13.09	6.09	27.00	19.60	1.38	4.48
$AlCl_3$						
0.0000	11.76	4.51	1.25	1.01	1.24	4.48
0.0001	11.54	−4.30	2.50	2.10	1.19	4.53
0.0005	11.51	−6.09	8.00	6.67	1.20	4.50
0.0010	11.85	−8.76	16.00	12.50	1.28	4.42

Note : L_{12}/T : Positive sign indicates electroosmotic flow from positive towards negative electrode and negative sign indicates its reverse.

TABLE 2—MEMBRANE CHARACTERISTICS FOR ZEOKARB–225 (H^+ FORM)/METHANOL-WATER SYSTEM ASCERTAINED FROM PERMEABILITY AND CONDUCTANCE DATA, AT 303±0 5 K.

Mole fraction of water	$L_{11}\times10^4$ ($cm^5 sec^{-1} dyne^{-1} K$)	$L_{12}\times10^6$ ($cm^3 sec^{-1} volt^{-1} K$)	$K\times10^7$ (mhos)	$\eta\times10^3$ (Poise)	$k\times10^3$ (mhos cm^{-1})	ϵ	$\frac{A}{l}\times10^1$ (cm)	$r\times10^4$ (cm)	$\zeta\times10^3$ (Volts)
0.1	3.18	5.33	2.85	5.67	2.280	35.7	1.25	6.14	3.19
0.2	2.70	4.73	3.00	6.67	2.375	38.0	1.26	6.13	2.45
0.3	2.24	4.18	3.30	7.44	2.451	40.5	1.35	5.72	2.13
0.4	1.84	2.91	3.65	8.74	2.637	43.5	1.38	5.43	1.57
0.5	1.76	2.85	3.80	9.84	2.801	47.3	1.36	5.67	1.62

TABLE 3—PHENOMENOLOGICAL-COEFFICIENTS, MEMBRANE CONSTANT, l_{11} AND l_{12} VALUES FOR DIFFERENT ZEOKARB-225 (H^+ FORM)/METHANOL SYSTEM : T=303±0.5 K.

Membranes	$L_{11}\times10^4$ ($cm^5 sec^{-1} dyne^{-1} K$)	$L_{12}\times10^8$ ($cm^3 sec^{-1} volt^{-1} K$)	$K\times10^7$ (mhos)	$k\times10^4$ (mhos cm^{-1})	$\frac{A}{l}\times10^1$ (cm)	$r\times10^4$ (cm)	$l_{11}\times10^8$ ($cm^4 dyne^{-1} sec^{-1} K$)	$l_{12}\times10^8$ ($cm^3 sec^{-1} volt^{-1} K$)
I	5.21	1.78	1.97	2.22	0.89	9.19	5.92	2.00
II	7.00	2.18	2.46		1.11	9.53	6.32	1.97
III	8.88	2.74	2.98		1.34	9.75	6.62	2.03

TABLE 4—PHENOMENOLOGICAL COEFFICIENTS, MEMBRANE CONSTANT AND MEMBRANE TRANSPORT COEFFICIENTS FOR ALUMINIUM OXIDE-METHANOL SYSTEM AT DIFFERENT TEMPERATURES.

T (K)	$L_{11}\times10^8$ ($cm^5 dyne^{-1} sec^{-1} K$)	$L_{12}\times10^9$ ($cm^3 sec^{-1} volt^{-1} K$)	$K\times10^5$ (mhos)	$k\times10^6$ (mhos cm^{-1})	$\frac{A}{l}$ (cm)	$r\times10^4$ (cm)	$l_{11}\times10^7$ ($cm^4 dyne^{-1} sec^{-1} K$)	$l_{12}\times10^8$ ($cm^3 sec^{-1} volt^{-1} K$)
298	1.007	4.470	0.150	6.766	0.22	8.18	4.54	2.02
303	1.130	5.907	0.165	7.381	0.22	8.26	5.05	2.64
308	1.269	7.548	0.180	7.791	0.23	8.28	5.49	3.27
313	1.408	8.919	0.190	8.200	0.23	8.41	6 08	3.85

A/l values in the case of pyrex membrane are reasonably constant. In the case of aluminium oxide membrane, the membrane constant is seen to be unaffected by temperature variation within the range of the present investigation. But, in the case of ion-exchange membrane, zeokarb-225, the membrane constant no longer remains constant. The ion-exchange meterials exhibit varied swelling when composition of the permeating liquid is varied. The observed increase in A/l is largely due to diminished swelling of the ion-exchanger in water rich mixtures.

Once the membrane constant is known it is possible to derive 'r' from hydrodynamic permeability data, since, according to Poisseuille's equation :

$$\left(\frac{J_v}{\triangle P}\right)_{\Delta\phi=0}=\frac{n\pi r^4}{8\eta l}=\frac{A}{l}\,\frac{r^2}{8\eta}$$

$$\text{or,}\quad r=\left(\frac{8\eta(J_v/\triangle P)_{\Delta\phi=0}}{A/l}\right)^{\frac{1}{2}} \qquad \ldots (3)$$

where, η is the viscosity of the permeant; J_v, the volume flux; $\triangle P$, the pressure difference and $\Delta\phi$, the electrical potential difference.

The derived value of r will of course be unambiguous, only, when the dimension of the permeant molecules is

much smaller than the openings within the membrane. The values of 'r' obtained by using the above equation are given in Tables 1, 2, 3 and 4, for pyrex, zeokarb-225 and aluminium oxide membranes.

The electrical character of a membrane permeant interface can be expressed in terms of zeta-potential, when $r \gg$ double layer thickness[9]. A knowledge of the membrane constant is also helpful in the estimation of zeta-potential, ξ, from electro-osmotic permeability data. According to the double layer picture electro-osmotic permeability is given by[10]

$$\left(\frac{J_v}{\Delta\phi}\right)_{\Delta P=0} = \frac{n\epsilon r^2 \xi}{4\eta l}$$

$$\text{or,}\quad \xi = \frac{4\pi\eta(J_v^0/\Delta\phi)_{\Delta P=0}}{\epsilon(A/l)} \qquad \dots (4)$$

where, ϵ is the dielectric constant of the permeant. $(J_v/\Delta\phi)_{\Delta P=0}$ has been found to be independent of $\Delta\phi$, upto 100 volts, in the case of electrolyte solutions. ξ, thus, remains unaltered when $\Delta\phi$ is varied within the range of investigation. ξ values obtained using equation (4) are given in Table 2, in the case of Zeokarb-225 membrane.

Transport phenomena through membranes under the simultaneous action of ΔP and $\Delta\phi$, on the basis of non-equilibrium thermodynamic theory, are given by[11,12]

$$J_v = L_{11}\left(\frac{\Delta P}{T}\right) + L_{12}\left(\frac{\Delta\phi}{T}\right) \qquad \dots (5)$$

$$I = L_{21}\left(\frac{\Delta P}{T}\right) + L_{22}\left(\frac{\Delta\phi}{T}\right) \qquad \dots (6)$$

$L_{ij}(i,j=1,2)$ are phenomenological coefficients. Onsager's reciprocity relationship established firmly[13-15] on the basis of experimental data on electrokinetic phenomena requires that $L_{12}=L_{21}$. It is obvious that

$$\left(\frac{J_v}{\Delta P}\right)_{\Delta\phi=0} = \frac{L_{11}}{T}\ ;\ \left(\frac{J_v}{\Delta\phi}\right)_{\Delta P=0}$$

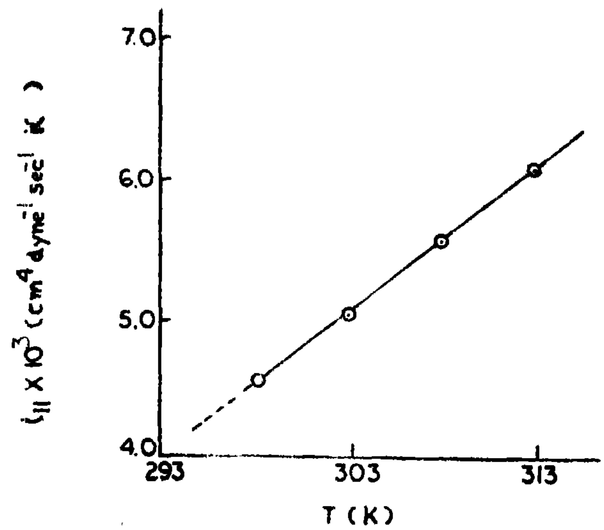
$$= \frac{L_{12}}{T}\ ;\ \text{and}\ \left(\frac{I}{\Delta\phi}\right)_{\Delta P=0} = \frac{L_{22}}{T} = K.$$

L_{11} and L_{12} values estimated from flux data, and the membrane conductance, $K = L_{22}/T$, from conductance data are, also included in Tables 1,2,3, and 4 for the pyrex, zeokarb-225 and alumina membranes.

It has been argued[16] that equation (5) may advantageously be written as

$$J_v = \frac{A}{l}\, l_{11}\left(\frac{\Delta P}{T}\right) + \frac{A}{l}\, l_{12}\left(\frac{\Delta\phi}{T}\right) \qquad \dots (7)$$

The phenomenological coefficients L_{11} and L_{12} have been estimated from hydrodynamic and electroosmotic permeability data for three different zeokarb-225, ion-exchange membranes, are included in Table 3 and for alumina membrane at different temperatures are included in table 4, along with membrane constant values. The values of the membrane transport coefficients l_{11} and l_{12}, are also given in Tables 3 and 4 for different zeokarb-225 membranes and alumina membrane at different temperatures. From Tables 3 and 4, it is seen that L_{11} and L_{12} are different for different membranes but l_{11} and l_{12} values are, however, fairly constant at a given temperature and unique for the membrane permeant system.



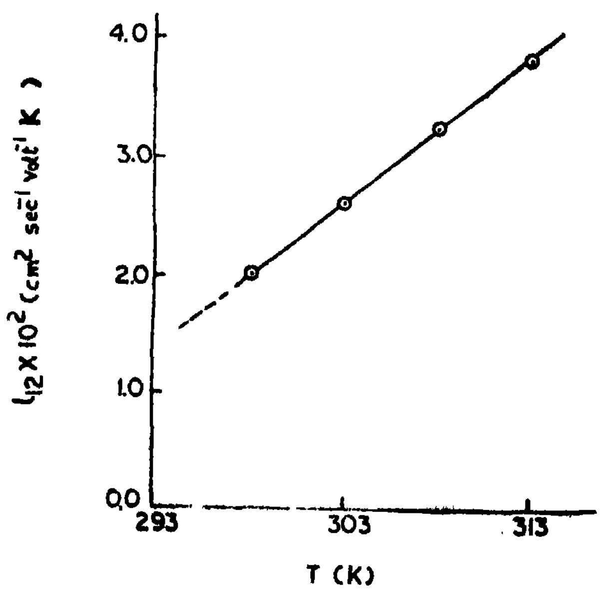


Fig. 1. Temperature dependence of the membrane transport coefficient, l_{11}.

Fig. 2. Temperature dependence of the membrane transport coefficient, l_{12}.

The plots given in Fig. 1 and Fig. 2, show that temperature dependence of these coefficients may be expressed as

$$l_{11} = \alpha_1 + \beta_1 T \quad \dots (8)$$

$$\text{and } l_{12} = \alpha_2 + \beta_2 T \quad \dots (9)$$

where; α_1, α_2, β_1 and β_2 are constants and T is temperature in K. From the plots of l_{11} vs. T., and l_{12} vs. T.,

$$\alpha_1 = -2.53 \times 10^{-2} \text{ cm}^4 \text{ dyne}^{-1} \text{ sec}^{-1} \text{ K.},$$

$$\beta_1 = 1.0 \times 10^{-4} \text{ cm}^4 \text{ dyne}^{-1} \text{ sec}^{-1},$$

$$\alpha_2 = -3.47 \times 10^{-1} \text{ cm}^2 \text{ sec}^{-1} \text{ volt}^{-1} \text{ K.},$$

$$\text{and } \beta_2 = 1.232 \times 10^{-3} \text{ cm}^2 \text{ sec}^{-1} \text{ volt}^{-1}.$$

References

1. R. P. Rastogi, Kehar Singh and M. L. Srivastava, *J. Phys. Chem.*, 1969, 73, 46.
2. R. P. Rastogi, Kehar Singh and S. N. Singh, *J. Phys. Chem.*, 1969, 73, 1593.
3. R. L. Blokhra and T. C. Singhal, *J. Phys. Chem.*, 1974, 78, 2302.
4. R. C. Srivastava and M. George Abraham, *J. Chem. Soc., Faraday Transactions I.*, 1976, 72, 2631.
5. R. P. Rastogi, Kehar Singh and J. Singh, *J. Phys. Chem.*, 1975, 79, 2574.
6. R. C. Srivastava and M. George Abraham, *J. Colloid & Interface Sci.*, 1976, 57(I), 58.
7. Vishnu and V. P. Mishra, *J. Carbohydrates Res.*, 1977, 59, 35.
8. R. P. Rastogi, *J. Sci. Ind. Res.*, 1969, 28, 284.
9. Kehar Singh and Raj Kumar, *Indian J. Chem.* (In press).
10. H. R. Kruyt "Colloid Science" Vol. I [Elsevier Pub. Co. Amsterdam] 1952.
11. S. R. DeGroot and P. Mazur, "Non-equilibrium Thermodynamics", (North-Holland Publishing Company, Amsterdam.), 1962.
12. A. Katchalsky and P. F. Curran, "Non-equilibrium Thermodynamics in Biophysics", [Harvard University Press, Cambridge, Mass.] 1965.
13. R. P. Rastogi, M. L. Srivastava and S. N. Singh, *J. Phys. Chem.*, 1970, 74, 2960.
14. M. L. Srivastava, *Indian J. Chem.*, 1971, 9, 48.
15. R. P. Rastogi and B. M. Misra, *Trans. Faraday Society*, 1967, 63(12), 540.
16. R. Haase, "Thermodynamics of Irreversible Processes", [Addison-Wesley Publishing Company, London], 1969.

J. Indian Chem. Soc.,
Vol. LVII, February 1980, pp. 208-211

Methylenation Studies of Desoxybenzoins : Characterisation of Minor Products and Debenzylation of Benzyloxyisoflavanones

M. L. MALIK and S. K. GROVER*

Department of Chemistry, University of Delhi, Delhi-110 007, India

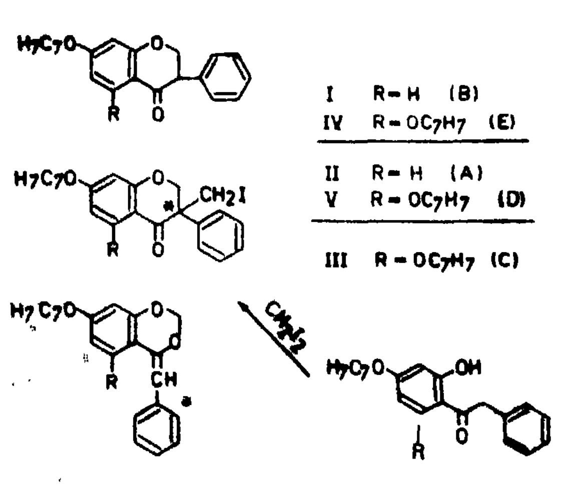
Manuscript received 19 March 1977, revised 16 April 1979, accepted 6 October 1979

The minor products in the reaction of 2-hydroxy-4-benzyloxydesoxybenzoin and methylene iodide are found to be corresponding enol-methylene ethers and 3-iodomethyl isoflavanones as shown by spectral studies. The latter compounds also form from the corresponding isoflavanones by reaction with methylene iodide under the same reaction conditions.

The best condition for debenzylation of benzyloxyisoflavanones is to heat with HCl : HOAc (1 : 2) at 60° for 10 min and for selective debenzylation in 5-position only for 2 min.

A reinvestigation of the synthesis of benzyloxyisoflavanones to afford hydroxyisoflavanones by methylene iodide method[1] has led to isolation and characterisation of minor products as presented below.

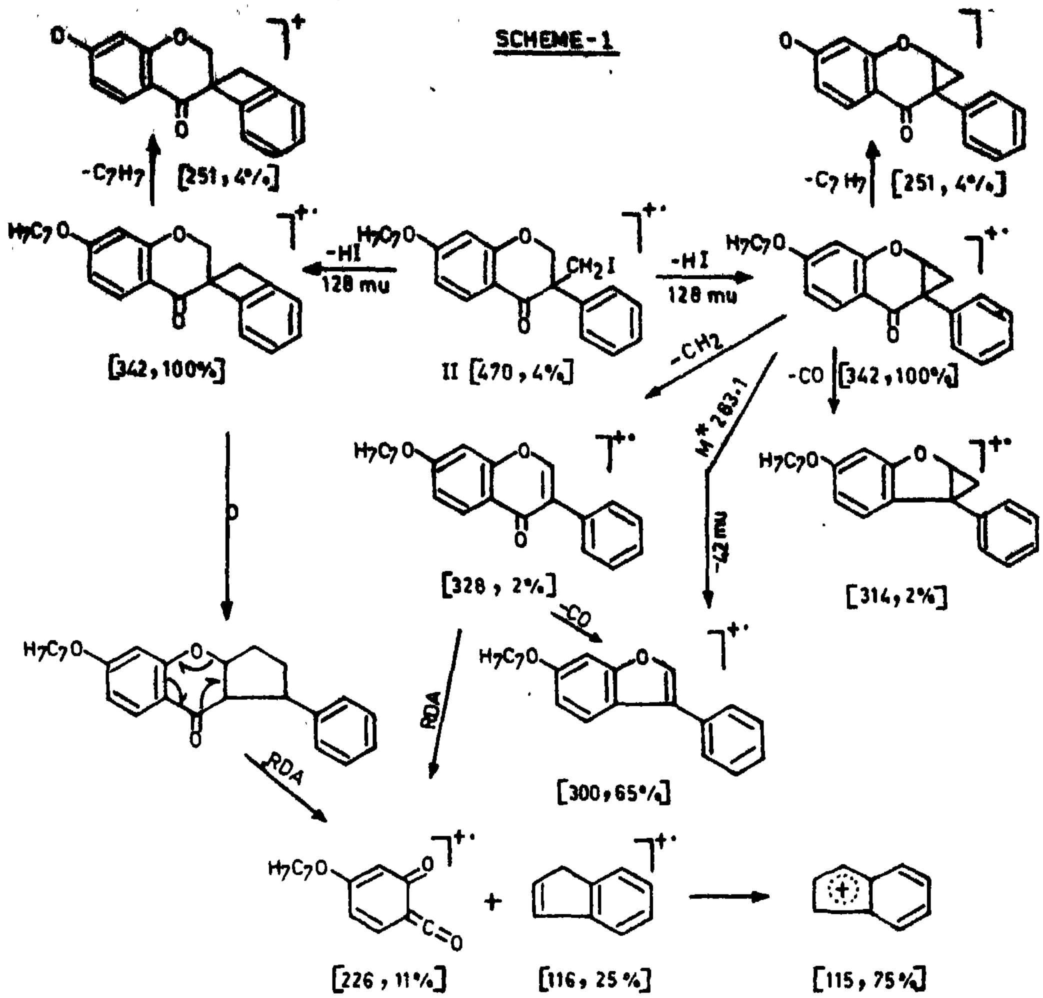
The crude product from reaction of 2-hydroxy-4-benzyloxy-phenyl benzyl ketone with methylene iodide[1] on careful chromatography over basic alumina gave two compounds 'A' and 'B' in addition to some impure fractions. Compound 'B' was identified as 7-benzyloxy isoflavanone(I)[1]. Compound 'A' did not give any colour with ethanolic ferric chloride showing that ortho hydroxy group in phenyl benzyl ketone had been involved in the reaction. It was found to contain iodine, an inference substantiated by the loss of 128 mass units (mu) equal to HI in the mass spectrum. NMR revealed the presence of iodomethyl group at δ 3.65 which appeared as an AB quartet (J 9 Hz) showing its presence on an asymmetric carbon atom, a quartet at δ 4.9 (J 9 Hz) and integrating for 2H showed the presence of $-O-CH_2-C^*$ (C^* being the asymmetric carbon) in addition to other protons due to rings A and C and the benzyloxy group at position 7. Compound 'A' was thus assigned the structure 7-benzyloxy-3-iodomethyl isoflavanone (II). This could form by nucleophilic substitution involving the carbanion, derived from product B, and methylene iodide. To confirm this view, 7-benzyloxy isoflavanone (I) was refluxed with methylene iodide under conditions of the above experiment, when the same compound 'A' was formed.



Various fragments in the mass spectra are rationalised for structure (II) as shown in scheme-I.

A parallel set of experiments with 2-hydroxy-4, 6-dibenzyloxy phenyl benzyl ketone gave three compounds C, D and E. Compound E, m.p. 180-81°, was identified as 5,7-dibenzyloxyisoflavanone from its spectral date and comparison with an authentic sample[1]. Compound D, m.p. 166-67° was assigned the structure, 5,7-dibenzyloxy-3-iodomethyl isoflavanone (V) on the basis of spectral data. Mass spectral fragmentation was similar to the one observed for structure II (Scheme I) except for certain subtle differences. This structure V was finally confirmed by converting 5,7-dibenzyloxyisoflavanone into compound D by reaction with methylene iodide under the conditions described in a similar case.

Compound C, m.p. 124-26°, gave negative ferric reaction but a positive gallic acid-sulphuric acid test indicating a methylene dioxy group in the molecule. The presence of a methylene dioxy group was confirmed by an absorption at δ 5.3 in NMR. It showed the molecular ion peak at m/e 436. IR showed the absence of carbonyl frequency which led to the conclusion that the reaction with methylene iodide had involved the *o*-hydroxyl and enol form of phenyl benzyl ketone to yield the compound C having structure (III). This structure is supported by its NMR spectrum.



Debenzylation Experiments :

Debenzylation of benzyloxyisoflavanones with hydrochloric acid-acetic acid mixture has been found to be complicated because of the instability of isoflavanone nucleus. Best results were obtained by using hydrochloric acid-acetic acid mixture in the ratio of (1:2) at 60° for 8-10 minutes. However, partial debenzylation of 5,7-dibenzyloxyisoflavanone could be accomplished in two minutes to get 7-benzyloxy-5-hydroxyisoflavanone.

Attempts at the synthesis of homoferreirin[2] by debenzylation of 5,7-dibenzyloxy-2', 4'-dimethoxyisoflavanone[1] by the above method were unsuccessful. This seems to be due to the additional complication arising from demethylation occurring at 2' position, which would account for the extremely complex nature of the reaction mixture.

Experimental

Melting points are uncorrected. UV spectra were taken in methanol solution using a Hilger spectrophotometer. Infrared spectra were taken on a Perkin Elmer Infracord 137. NMR spectra were taken on 60 MHz Varian and 100 MHz JEOL spectrometers using tetramethylsilane as internal standard. Gallic acid-sulphuric acid test was taken as positive when an emerald-green colour appeared on heating at 80-90°.

7-Benzyloxy-3-iodomethyl isoflavanone (*A*) :

A mixture of 2-hydroxy-4-benzyloxyphenyl benzyl ketone[1] (1.5 g), methylene iodide (1.5 ml), potassium carbonate (10.0 g) and acetone (150 ml) was refluxed for 150 hr. The solvent was distilled off, water added and alkaline solution extracted with ether. Ether residue was treated with water and steam distilled to remove excess methylene iodide. The aqueous solution was once again extracted with ether and ether residue dried in vacuum over P_2O_5. The crude product was column chromatographed over basic alumina (50.0 g) using petroleum ether, petroleum ether-benzene (3:1) mixtures as eluents and fractions (50 ml each) collected and studied in TLC. Homogenous fractions were mixed and subjected to crystallisation when the following products were isolated.

(i) 7-Benzyloxy-3-iodomethyl isoflavanone (A) (II) was obtained from petroleum ether-benzene eluates

(fractions 3 to 10) as colourless shining prisms (0.13 g), m. p. 167-68°, λ_{max}^{MeOH} 280, 315 nm (log ε 4.18 & 3.92 respectively) ; ν_{max}^{KBr}(>C=0) 1680 cm⁻¹ ; M^+ 470 (Found ; C, 58.12 ; H, 4.30. $C_{23}H_{19}O_3I$ requires C, 58.09 ; H. 4.04%).

The same product was obtained when 7-benzyloxy-isoflavanone (0.15 g) in acetone (30.0 ml), methylene iodide (0.15 ml) and potassium carbonate (2 g) was refluxed for 65 hr.

(ii) 7-Benzyloxyisoflavanone (B) (I) was obtained from petroleum ether-benzene (3:1) eluates (fractions 16 to 36) as colourless shining plates (0.3 g) (from benzene-petroleum ether) m.p. 130-31°. Lit[1]. m.p. 130-31°. It gave identical values of UV, IR and NMR data as recorded in lit[1].

Methylenation products of 2-hydroxy-4,6-dibenzyloxyphenyl benzylketone :

A solution of 2 - hydroxy - 4, 6 - dibenzyloxyphenyl benzyl ketone (2.0 g), methylene iodide (2.0 ml) in acetone (200 ml) was refluxed with potassium carbonate (20.0 g) for 150 hr. The reaction mixture was worked up as described earlier. 5,7-Dibenzyloxyisoflavanone (E) separated on maceration of crude product with ether. It was filtered and crystallised from benzene-petroleum ether mixture as colourless needles (0.8 g), m.p. 180-81° ; lit[1]. m.p. 180-81°. It gave identical values of UV, IR and NMR data as recorded in lit[1].

4,6-Dibenzyloxy-α:2-methylenedioxystilbene (III) :

The above ether residue was chromatographed over basic alumina using petroleum ether, benzene-petroleum ether (1:9) and benzene-petroleum ether (1:3) mixtures.

Petroleum ether eluates on concentration gave an impure product. The crude product was purified by preparative TLC using silica gel as adsorbent and benzene-ethyl acetate (9:1) mixture as solvent system. Bands at R_f 0.72 were cut and eluted with ethyl acetate which on concentration gave enol methylene ether (III) (15 mg), m.p. 124-26° (from benzene-petroleum ether) λ_{max}^{MeOH} 300 nm, M^+ 436. It gave negative ferric reaction but positive gallic acid-sulphuric test for methylene dioxy group.

NMR ($CDCl_3$) : δ 4.95 & 5.1 (2H each, s,-O-CH_2-Ph at C5 & C7) 5.3 (2H, s,-O-CH_2-O-), 6.15 (2H, m, H6 & H8) ; 6.9 (1H, s, =*CH*−C_6H_5) and between 7.2 and 7.6 (15H, m, 10 aromatic of -O-CH_2-C_6H_5 at C5 and C7 and 5 aromatic protons of =CH-C_6H_5).

5,7-Dibenzyloxy-3-iodomethyl isoflavanone (V):

Petroleum ether-benzene (9:1) eluates on concentration afforded an impure product. A major product having R_f 0.62 on silica gel and benzene-ethyl acetate (9:1) as solvent system was purified by preparative TLC, when 5,7-dibenzyloxy-3-iodomethyl isoflavanone (D) was obtained as colourless crystals (20 mg) m.p. 166-67° (from benzene-petroleum ether), λ_{max}^{MeOH} 290 nm, $\nu_{(>C=O)max}^{KBr}$ 1670 cm⁻¹. It gave negative ferric and negative gallic acid-sulphuric acid tests.

M^+576 (2%), 448 (100%), 406 (26%), 332 (2%), 116(2%) and 115 (8%).

NMR $CDCl_3$) : δ 4.1 (2H, AB q, J 9Hz, −CH_2I at C−3) ; between 4.6 and 5.0 (6H, m, 2H, of −OCH_2 −C* (C* being asymmetric carbon atom) and 4H of O−CH_2−C_6H_5 at C5 and C7 respectively ; between 6.4 and 7.4 (17H, m, 15 aromatic protons of side phenyl and two −O−CH_2−C_6H_5 and 2H of H6 and H8).

7-Hydroxyisoflavanone :

7-Benzyloxyisoflavanone (30.0 mg) was dissolved in glacial acetic acid (5.0 ml) by warming at 60° and conc. hydrochloric acid (2.5 ml) added dropwise. The mixture was shaken at the above temperature for 10 minutes, and worked up as usual. The product on crystallisation from aq. methanol gave 7-hydroxyisoflavanone as colourless crystals (8.0 mg), m.p. 173-5°, lit[8]. m.p. 175° ; λ_{max}^{MeOH} 275, 315 nm (log ε 5.17 & 3.99 respectively). $\nu_{(>C=O)}\frac{KBr}{max}$ 1670 cm⁻¹.

7-Benzyloxy-5-hydroxyisoflavanone :

5,7-Dibenzyloxyisoflavanone (50 mg) was dissolved in glacial acetic acid (5.0 ml) at 60° and conc. hydrochloric acid (2.5 ml) added dropwise. A yellow colour appeared and after two minutes at this temperature a solid crystallised out. On usual working up and crystallisation of the residue from aq. methanol afforded 7-benzyloxy-5-hydroxyisflavanone as colourless solid (20 mg), m.p. 134-35°. λ_{max}^{MeOH} 290 nm (log ε 3.99) $\nu_{(>C=O)\,max}^{KBr}$ 1645 cm⁻¹).

NMR ($CDCl_3$) : δ 3.9 (1H, t, J 7Hz, H3) ; 4.65 (2H, d, J 7Hz, CH_2 at C2) ; 5.1 (2H, s, $-O-CH_2-C_6H_5$ at C7) ; 6.3 (2H, m, H6 & H8) ; between 7.28 – 7.9 (10H, m, 5H, of side phenyl ring and 5 aromatic protons of $-O-CH_2-C_6H_5$) and 12.8 (1H, s, chelated -OH at C5).

5,7-Dihydroxyisoflavanone :

5,7-Dibenzyloxyisoflavanone (30 mg) or 7-benzyloxy-5-hydroxyisoflavanone (20 mg) was treated with acetic acid (3.0 ml) and hydrochloric acid (2.5 ml) as described above. The product on crystallisation from aq. methanol gave 5,7-dihydroxy-isoflavanone (2.0 mg), m.p. 166-65°. Lit[4] m.p. 163-5°. λ_{max}^{MeOH} 290 nm (log ε 4.31) ; $\nu_{(>C=O)\,max}^{KBr}$ 1645 cm^{-1}.

References

1. S. K. Aggarwal, S. K. Grover and T. R. Seshadri, *Indian J. Chem.*, 1972, 10, 804.
2. F. E. King and K. G. Neill, *J. Chem. Soc.*, 1952, 4752.
3. N. Inoue, *J. Chem. Soc., Japan*, 1958, 79, 112.
4. N. Inoue, *Nippon Kagaku Zassi*, 1958, 79, 1537.

J. Indian Chem. Soc.,
Vol. LVII, February 1980, pp. 212-215

Synthesis of Antifungal Pyrazolones and Related Compounds

S. P. SUMAN AND S. C. BAHEL

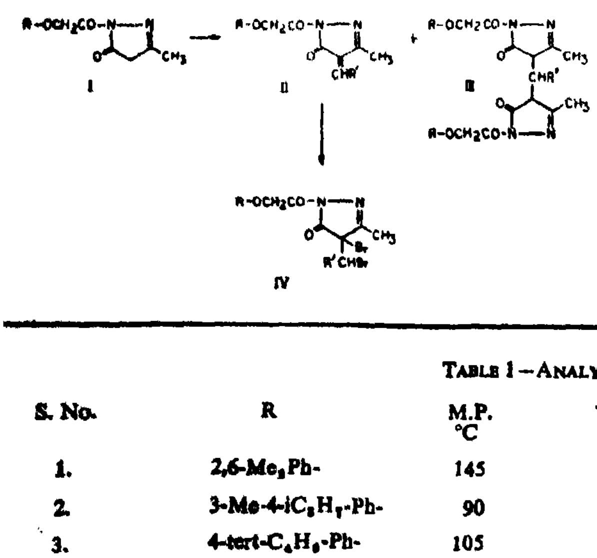
Chemistry Department, University of Gorakhpur, Gorakhpur (U. P.)

Manuscript received 12 February 1979, revised 12 September 1979, accepted 9 January 1980

Three N_1-aryloxyacetyl-3-methyl-5-pyrazolones, twenty 4-arylidene-N_1-aryloxyacetyl-3-methyl-5-pyrazolones, twenty bis(N_1-aryloxyacetyl-3-Me-5-pyrazolone-5-yl) arylmethanes and eighteen 4-bromo-(4-α-bromoaryl)-N_1-aryloxyacetyl-3-methyl-5-pyrazolones have been synthesised with a view to study their antifungal activity. Some of the compounds have been screened for their antifungal activity against '*A niger*' and '*A. flavus*' and found to be antifungal.

THERAPEUTICAL importance of pyrazolone and its derivatives has been studied by several investigators as bactericides and fungicides[1,2]. Some halogenated and non-halogenated pyrazolones have been screened as fungicides[3,4]. Working on the generalization that N-heterocycles incorporated with CO group show significant pesticidal activity[5,6], we have prepared the title compounds which possess an additional CO group directly linked with the pyrazolone ring leading thereby to a possible enhanced activity.

N_1-Aryloxyacetyl-3-methyl-5-pyrazolones(I) required in this work, have been obtained by the reaction of aryloxyacetyl-hydrazines with ethyl acetoacetate[7]. Reaction of (I) with arylaldehyde in glacial acetic acid gave their monoarylidene derivatives (II) along with bis-pyrazolone compounds (III), which were isolated by diluting the solution after separation of (II). The monoarylidene compounds (II) obtained were brominated with bromine in acetic acid to give 4-bromo-(4-α-bromoaryl)-N_1-aryloxyacetyl-3-methyl-5-pyrazolones(IV).



The analytical data of compounds, thus obtained are summarised in Tables 1-4.

Experimental

All the melting points are uncorrected.

Aryloxyacetylhydrazines :

These were prepared by the method of L. Conti[8].

N_1-Aryloxyacetyl-3-methyl-5-pyrazolones[7] *(I)* :

To an ethanolic suspension (20 ml) of aryloxyacetylhydrazine (0.01*M*), ethylacetoacetate (0.01*M*) was added and the mixture refluxed for three hours. On evaporation a solid was obtained which was washed and crystallised.

4-Arylidene-N_1-aryloxyacetyl-3-methyl-5-pyrazolones (II) :

An arylaldehyde (0.01*M*) was dissolved in glacial acetic acid (5ml). This was added to a glacial acetic acid

TABLE 1—ANALYTICAL DATA OF (I)

S. No.	R	M.P. °C	Yield %	Molecular formula	N% Found	N% Calcd.
1.	2,6-Me_2Ph-	145	90	$C_{13}H_{14}N_2O_3$	12.00	12.00
2.	3-Me-4-iC_3H_7-Ph-	90	87	$C_{15}H_{20}N_2O_3$	10.62	10.76
3.	4-tert-C_4H_9-Ph-	105	80	$C_{15}H_{20}N_2O_3$	10.68	10.76

All the compounds gave satisfactory analysis for C and H.

TABLE 2—ANALYTICAL DATA OF (II)

S. No.	R	M.P. °C	Yield %	Molecular formula	N% Found	N% Calcd.
			R = 2,6-Me$_2$-Ph-			
1.	Ph-	185	55	$C_{20}H_{20}N_2O_2$	8.70	8.75
2.	2-Cl-Ph-	170	60	$C_{20}H_{19}ClN_2O_2$	—	7.89
3.	3-Cl-Ph-	164	55	$C_{20}H_{19}ClN_2O_2$	7.84	7.89
4.	4-Cl-Ph-	181	62	$C_{20}H_{19}ClN_2O_2$	7.80	7.89
5.	2-OH-Ph-	160	50	$C_{20}H_{20}N_2O_3$	8.21	8.33
6.	3-OH-Ph-	150	42	$C_{20}H_{20}N_2O_3$	—	8.33
7.	4-OH-Ph-	175	53	$C_{20}H_{20}N_2O_3$	8.25	8.33
8.	4-Me$_2$N-Ph-	139	44	$C_{22}H_{25}N_3O_2$	11.51	11.57
9.	4-CH$_3$O-Ph-	145	48	$C_{21}H_{22}N_2O_3$	7.91	8.00
10.	PhCH=CH-	133	40	$C_{22}H_{22}N_2O_2$	8.03	8.11
			R = 3-Me-4-iC$_3$H$_7$-Ph-			
11.	Ph-	170	50	$C_{22}H_{24}N_2O_2$	—	8.04
12.	2-Cl-Ph-	162	50	$C_{22}H_{23}ClN_2O_2$	—	7.32
13.	3-Cl-Ph-	154	47	$C_{22}H_{23}ClN_2O_2$	—	7.32
14.	4-Cl-Ph-	159	52	$C_{22}H_{23}ClN_2O_2$	7.30	7.32
15.	2-OH-Ph-	165	50	$C_{20}H_{24}N_2O_3$	7.60	7.69
16.	3-OH-Ph-	142	42	$C_{20}H_{24}N_2O_3$	—	7.69
17.	4-OH-Ph-	150	54	$C_{20}H_{24}N_2O_3$	—	7.69
18.	4-Me$_2$N-Ph-	135	48	$C_{24}H_{29}N_3O_2$	10.70	10.74
19.	4-MeO-Ph-	150	42	$C_{23}H_{26}N_2O_3$	7.33	7.40
20.	Ph-CH=CH	120	35	$C_{24}H_{26}N_2O_2$	7.42	7.50

– not analysed.

TABLE 3—ANALYTICAL DATA OF (III)

S. No.	R′	M.P. °C	Yield %	Molecular formula	N% Found	N% Calcd.
			R = 2,6-Me$_2$Ph-			
1.	Ph-	160	40	$C_{31}H_{34}N_4O_4$	10.02	10.14
2.	2-Cl-Ph-	150	33	$C_{31}H_{33}ClN_4O_4$	9.50	9.54
3.	4-Cl-Ph-	170	35	$CC_{31}H_{33}ClN_4O_4$	—	9.54
4.	4-Cl-Ph-	170	35	$C_{31}H_{33}ClN_4O_4$	—	9.54
5.	2-OH-Ph-	140	35	$C_{31}H_{34}N_4O_5$	9.81	9.85
6.	3-OH-Ph-	132	30	$C_{31}H_{34}N_4O_5$	—	9.85
7.	4-OH-Ph-	158	38	$C_{31}H_{34}N_4O_5$	9.79	9.85
8.	4-Me$_2$-N-Ph-	130	40	$C_{33}H_{41}N_5O_4$	—	11.76
9.	4-MeO-Ph-	120	42	$C_{34}H_{36}N_4O_5$	9.53	9.62
10.	Ph-CH=CH-	101	40	$C_{33}H_{37}N_4O_4$	9.67	9.70

Contd.

Table 3 Contd.

S. No.	R′	M.P. °C	Yield %	Molecular Formula	N% Found	N% Calcd.
			R = 3-Me-4-iC$_3$H$_7$-Ph-			
11.	Ph-	155	42	$C_{35}H_{40}N_4O_4$	9.15	9.21
12.	2-Cl-Ph-	148	36	$C_{35}H_{39}ClN_4O_4$	—	8.71
13.	3-Cl-Ph-	140	30	$C_{35}H_{39}ClN_4O_4$	8.61	8.71
14.	4-Cl-Ph-	152	35	$C_{35}H_{39}ClN_4O_4$	—	8.71
15.	2-OH-Ph-	135	42	$C_{35}H_{40}N_4O_5$	8.91	8.97
16.	3-OH-Ph-	120	35	$C_{35}H_{40}N_4O_5$	—	8.97
17.	4-OH-Ph-	143	40	$C_{35}H_{40}N_4O_5$	—	8.97
18.	4-Me$_2$N-Ph-	115	33	$C_{37}H_{45}N_5O_4$	10.90	10.92
19.	4-MeO-Ph-	114	43	$C_{36}H_{42}N_4O_5$	8.71	8.77
20.	Ph-CH = CH-	105	42	$C_{37}H_{42}N_4O_4$	8.80	8.84

—not analysed.

TABLE 4—ANALYTICAL DATA OF (IV)

S. No.	R′	M.P. °C	Yield %	Molecular formula	N% Found	N% Calcd.
			T = 2,6-Me$_2$Ph-			
1.	Ph-	135	90	$C_{30}H_{30}Br_2N_2O_2$	6.77	5.83
2.	2-Cl-Ph-	120	92	$C_{30}H_{29}Br_2ClN_2O_2$	5.41	5.44
3.	3-Cl-ph-	110	90	$C_{30}H_{29}Br_2ClN_2O_2$	—	5.44
4.	4-Cl-Ph-	126	95	$C_{30}H_{29}Br_2ClN_2O_2$	—	5.44
5.	2-OH-Ph-	110	82	$C_{30}H_{30}Br_2N_2O_3$	5.59	5.64
6.	3-OH-Ph-	90	70	$C_{30}H_{30}Br_2N_2O_3$	5.57	5.64
7.	4-OH-Ph-	113	90	$C_{30}H_{30}Br_2N_2O_3$	—	5.64
8.	4-Me$_2$N-Ph-	85	74	$C_{32}H_{35}Br_2N_3O_2$	8.00	8.03
9.	4-MeO-Ph-	76	87	$C_{31}H_{32}Br_2N_2O_3$	5.43	5.49
			R = 3-Me-4-iC$_3$H$_7$-Ph-			
10.	Ph-	115	92	$C_{33}H_{36}Br_2N_2O_2$	5.47	5.51
11.	2-Cl-Ph-	104	96	$C_{33}H_{35}Br_2ClN_2O_2$	5.11	5.16
12.	3-Cl-Ph-	92	80	$C_{33}H_{35}Br_2ClN_2O_2$	—	5.16
13.	4-Cl-Ph-	109	89	$C_{33}H_{35}Br_2ClN_2O_2$	—	5.16
14.	2-OH-Ph-	84	78	$C_{33}H_{36}Br_2N_2O_3$	5.24	5.34
15.	3-OH-Ph-	78	90	$C_{33}H_{36}Br_2N_2O_3$	5.28	5.34
16.	4-OH-Ph-	93	84	$C_{33}H_{36}Br_2N_2O_3$	—	5.34
17.	4-Me$_2$N-Ph-	70	80	$C_{35}H_{41}Br_2N_3O_2$	7.70	7.76
18.	4-MeO-Ph-	74	86	$C_{34}H_{38}Br_2N_2O_3$	5.12	5.20

All the compounds gave satisfactory analysis for bromine.
—not analysed.

(15 ml) solution of N_1-aryloxyacetyl-3-methyl-5-pyrazolone (0.01 M) and resulting solution kept in a refrigerator until a product separated out (1 hr to 20 days). It was filtered, washed with cold glacial acetic acid, water and crystallised with methanol.

Arylidene bis-pyrazolones(III) [*Bis-(N_1-aryloxyacetyl-3-Me-5-pyrazolone-5-yl)-arylmethane*][9] :

After separating the (II), the filtrate was diluted with water and the solution kept in the refrigerator until a product separated out (at 12 to 30 hours). It was filtered, washed with water, dried and crystallized with methanol.

4-Bromo-(4-α-bromoaryl)-N_1-aryloxyacetyl-3-methyl-5-pyrazolones (IV) :

To the suspension of 4-arylidene-N_1-aryloxyacety'-3-methyl-5-pyrazolone (0.005*M*) in acetic acid (20 ml), bromine in acetic acid was added dropwise with constant stirring till the color of bromine persisted. The mixture was kept overnight, when a solid separated out. It was filtered, washed with water, dried and crystallised with methanol.

Fungicidal activity :

All the compounds of Table 1, ten compounds (1, 2, 5, 8, 9, 10, 13, 17, 18 and 20) of Table 2, nine compounds of Table 3 (1, 3, 7, 8, 10, 14, 17, 18 and 20) and nine compounds of Table 4 (1, 3, 5, 8, 9, 11, 14, 17 and 28) were screened for their antifungal activity against '*A. niger*' and '*A. flavus*' by agar plate technique[10,11] at three different concentrations namely, 1:1,000, 1:10,000 and 1:100,000. The compounds screened were found to show antifungal activity. All the compounds derived from pyrazolones show higher fungicidal activity than the parent compounds. In general, antifungal activity has been found to increase in the order I, II, III, IV. The different groups of the aldehyde moiety do not show any significant effect towards the antifungal activity.

Acknowledgement

Authors are thankful to Prof. R. P. Rastogi, Head, Chemistry Department, University of Gorakhpur, Gorakhpur for departmental facilities.

References

1. G. B. Crippa and S. Maffei, *Gazz. Chelm. Etal.*, 1942, **72**, 67.
2. Chatterjee and Ghosh, *Proc. Asiatic Soc. Bengal*, 1919, 15.
3. B. Nanda, S. Padmanavan, B. Tripathi and A. S. Misra, *J. Indian Chem. Soc.*, 1975, **52**, 533.
4. A. Nayak, S. Das, C. R. Misra and A. S. Misra, *J. Indian Chem. Soc.*, 1977, **54**, 485.
5. Horsfall and Rich, *Contribs. Boyce Thompson, Inst.*, 1951, **16**, 313.
6. S. P. Suman and S. C. Bahel, *J. Indian Chem. Soc.*, 1979, **56**, 374.
7. M. Wolf, *Chem. Abs.*, 1968, **68**, 49599v.
8. L. Conti, *Chem. Abs.*, 1964, **61**, 4253e.
9. P. N. Dhal, T. E. Achary, A. Nayak and M. K. Rout, *J. Indian Chem. Soc.*, 1973, **50**, 680.
10. J. G. Horshafall, *Bot. Rev.*, 1845, **5**, 357.
11. U. S. D. A. Circular No. 198, 1931.

J. Indian Chem. Soc.,
Vol. LVII, February 1980, pp. 216-218

Molecular Complexes of Dichloro-*p*-Benzoquinone Derivatives with Aromatic Amines

Y. M. ISSA, A.E. EL-KHOLY, A.M. HINDAWEY and R. M. ISSA

Chemistry Department, Faculty of Education, King Abdulaziz University, Mecca, Saudi Arabia

Manuscript received 21 April 1979, accepted 25 December 1979

Molecular complexes of substituted anilines with chloranilic acid (I) and dichloro-dicyano-*p*-benzoquinone (II) are prepared and investigated by infrared spectroscopy. Anilines substituted at the aromatic ring form two types of compounds involving either a π-π^* interaction or a proton transfer besides the π-π^* C.T. with I while II formed the anilide. N-Substituted anilines form compounds involving π-π^* C.T. or π-π^* and n-π^* interactions depending on the electronic character of the substituent on the N-atom.

MOLECULAR complexes (M.C.) of the donor-acceptor type can be readily formed between aromatic amines and halogen derivatives of *p*-benzoquinone. The previous studies were mainly confined to the tetrahalogen derivatives chloranil[1], bromanil[2] and iodoanil[3]. The investigation of these molecular compounds was carried out using uv-and ir-absorption spectroscopy. The former method was utilised for the determination of the ionisation potentials of several donor molecules[4].

The present article includes the results of an infrared spectroscopic investigation of the molecular complexes prepared by the interction of 2,5-dichloro-3,6-dihydroxy-*p*-benzoquinone (chloranilic acid) (I) or 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (II) with aromatic amines.

The N-substituted anilines are : a) N-methyl aniline, b) N-ethyl aniline, c) N-dimethyl aniline, d) diphenylamine, e) N-acetyl aniline, f) N-methyl anthranilic acid, g) N-dimethyl-*p*-aminobenzaldehyde, h) N,N,N',N'-tetramethyl-*p*-phenylenediamine.

Experimental

The chemicals used in the present investigation were pure laboratory grade chemicals from (BDH).

The molecular complexes were prepared by mixing a hot saturated solution of the donor (0.01 mole) in absolute ethanol with an identical one of the acceptor. The solid M. C. separated on mixing or on standing. In the former case, the compounds were purified by boiling with ethanol to ensure freeing from unreacted products. In the latter case, the M.C. were purified by crystallisation. The yield amounts to 90-95% for insoluble compounds and 70-80% for the soluble ones.

Elemental analysis for a series of molecular compounds revealed the formation of 1:1 (donor : acceptor) complexes.

The ir-spectra were recorded, in the solid state applying the KBr disc method, on a Unicam SP 1000 infrared spectrophotometer. Some spectra were obtained by the aid of the Beckman IR-4 spectrophotometer.

Results and Discussion

On allowing the acceptors used in the present investigation to react with aromatic amines (aniline or its phenyl substituted derivatives), only chloranilic acid formed molecular compounds. Chloranil and dichlorodicyano benzoquinone formed anilide derivatives, the ir-spectra of these compounds showed an intense band at 3200-3250 cm^{-1} corresponding to the stretching mode of a secondry amino group[5]. The formation of anilides in case of II can be ascribed to the existence of four acceptor substituents on the quinone nucleus which increases the reactivity of the chlorine atoms. On the other hand, the presence of the OH-groups in I can deactivate the chlorine atoms through their donor character. Accordingly, the molecular complexes of aniline and its phenyl substituted derivatives are confined to chloranlic acid only. To avoid the anilide formation with dichlorodicyano benzoquinone recourse was taken to investigate the molecular compounds with N-substituted anilines.

(*A*) *Molecular Compounds of Anilines with Chloranilic acid* :

The reaction of chloranilic acid with anilines leads to the formation of two types of compounds depending on the basicity of the aniline derivative used. This is gathered from the difference in the changes of the spectra of the two types (Fig. 1).

i-Compounds involving π-π^* bonding :

This type of molecular compounds takes place with low basicity anilines (pk$_a \geq 3.0$). The spectra of this class can be considered as an overlap of the spectra of the components with some shifts in the bands. The two ν_{OH} bands of chloranilic acid at 3235 and 3120 cm^{-1} are generally shifted to lower wavenumbers which is also the case for the two carbonyl bands at 1670 and and 1637 cm^{-1}. This shift indicates a stronger intramolecular hydrogen bonding in the molecular complex in comparison to the free chloranilic acid molecule.

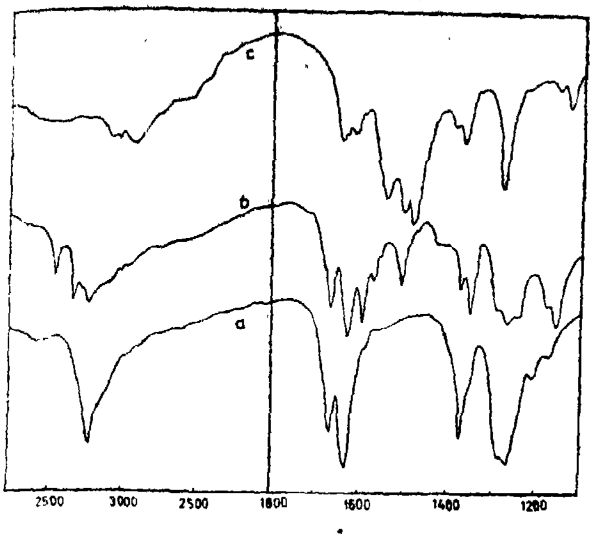


Fig. I. ir-spectra of chloranilic acid and its molecular complexes with phenyl substituted anilines.

a) chloranilic acid. b) *o*-NO_2-aniline complex. c) 2,4-di-Cl-aniline complex.

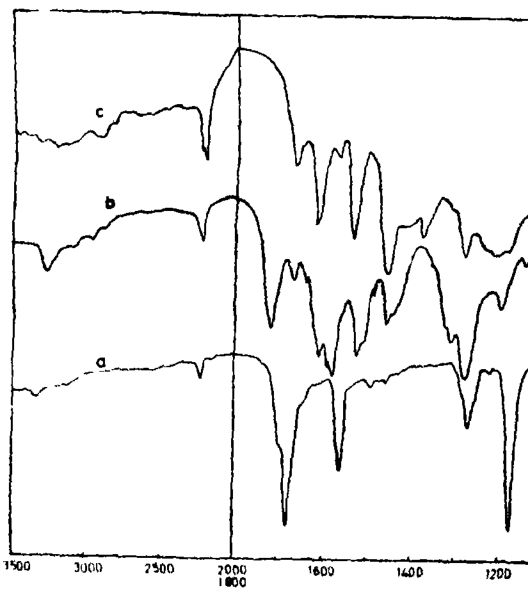


Fig. II. ir-spectra of dichloro-dicyano-*p*-benzoquinone and its molecular complexes with N-substituted anilines.

a) dichloro-dicyano-*p*-benzoquinone
b) N-acetyl aniline complex.
c) N, N, N′, N′-tetramethyl *p*-phenylenediamine complex.

The stronger hydrogen bonding in the molecular complex is substantiated by the shift of the δ_{OH} bands at 1290 and 1270 cm^{-1} to higher wavenumbers[6] and those of the ν_{C-OH} at 1212 and 1170 cm^{-1} to lower values. The strengthening of the intramolecular hydrogen bonding in the molecular complex results from the intermolecular charge transfer from the aniline molecule as donor to chloranilic acid as acceptor. This involves the location of a π-electron from the highest filled orbital on the anilino ring to the lowest vacant level on the ring of chloranilic acid i.e. π-π^* type.

The occurence of the intermolecular charge transfer is gathered from the shift of the γ_{CH} bands of the donor molecules to higher wavenumbers[7-9]. The ν_{NH_2} bands display also a slight shift to higher wavenumbers indicating a decrease of the electron density on the aniline ring.

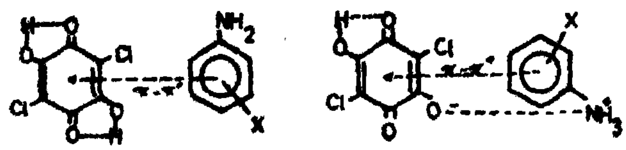
II-Molecular compounds comprising proton transfer and π-π^* bonding :

These molecular compounds display large changes in their spectra compared to those of their components. The ν_{OH} band of chloranilic acid at 3235 cm^{-1} and the ν_{NH_2} bands of the anilines within the 3300-3500 cm^{-1} range are no more observed in the spectra of these molecular compounds. Instead of these bands, a series of broad intense bands appear within the 3000-2400 cm^{-1} with broad peaks at 2920-2840, 2740-2680 and 2640-2580 cm^{-1}. These bands correspond to the stretching mode of the N-H groups in the anilinium ion[10], hence the second type of molecular compounds would involve the transfer of a proton from one OH-group of chloranilic acid to the NH_2-group of the aniline derivative. The disappearance of the ν_{OH} bands at 3235 cm^{-1} is accompanied by the vanishing of the two bands at 1290 and 1212 cm^{-1} due to the δ_{OH} and ν_{C-OH} modes.

The C=O bands shift to lower wavenumbers with the higher frequency band displays a large shift such that it interacts stronglys with the other C=O band. In some cases the low frequency C=O band appears as a shoulder or intermingles with the other C=O band forming a single broad band. The apparent lowering of the C=O band can be explained by the strong polarising influence of the neighbouring phenate ion.

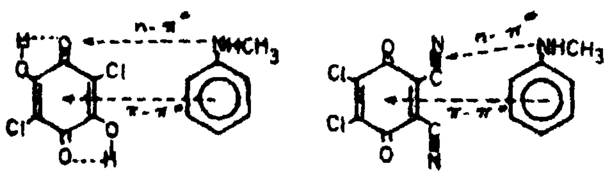
The OH-bands at 3120 and 1170 cm^{-1} are shifted to lower wavenumbers while that at 1270 cm^{-1} display the oposite behaviour. This is analogous to the shifts observed with the first class of molecular compounds and can be explained in the same manner i.e. increased strength of the intramolecular hydrogen bonding involving the remaining OH-group as a result of the intermolecular $\pi-\pi^*$ C. T. interaction. The existence of the $\pi-\pi^*$ interaction is supported by the shift of the γ_{CH} bands of the donor molecules to higher wavenumbers. Thus the bonding in this class involves the $\pi-\pi^*$ interaction and an electrostatic attraction between the positive and negative charges on the ions forming the molecular complex. Based on the above,

the two types of molecular compounds can be formulated as follows :



$\pi-\pi^*$ complexes (i) $\pi-\pi^*$ + proton transfer complexes (ii)

This shift indicates a certain differentiation in the energies of the two C≡N groups; one C≡N group would suffer an increased polarisation under the influence of the $\pi-\pi^*$ interaction, hence being displayed to lower energies. The otherr C≡N group being shifted to higher wavenumbers would be involved in $n-\pi^*$ interaction with the amino nitrogen of the donor molecule. Thus the substituted amino group would face the C≡N group. Based on these information, compounds involving $n-\pi^*$ interaction can be formulated as follows :



(B) *Molecular Compounds of N-Substituted anilines* :

Chloranilic acid reacts with the N-substituted anilines under investigation, except N-ethyl aniline, forming molecular complexes involving intermolecular charge transfer. N-ethyl aniline on the other hand froms molecular complex of the charge and proton transfer type. This is gathered from a comparison of the spectral shifts in case of N-substituted anilines with those of phenyl substituted anilines.

The most striking effect is the shift of the higher frequency C=O band to higher wavenumbers in the spectra of molecular complexes of a, c and g. This shift recalls the behaviur of C. T. complexes of aromatic nitrocompounds with aniline derivatives involving an $n-\pi^*$ transition[7-9]. Thus the shift of the carbonyl band to higher wavenumbers can be ascribed to the occurance of an $n-\pi^*$ interaction. This involves the location of an n-electron from the amino nitrogen to the lowest vacant π-level on the C=O group. This premise is substantiated by the shift of both C=O bands to higher values in case of tetramethyl-*p*-phenylenediamine where the two carbonyl groups of chloranilic acid face two dimethyl amino groups. The $n-\pi^*$ interaction is not possible in case of d and e due to the presence of an acceptor group attached to the nitrogen atom. For f the participation of the lone pair of the nitrogen atom in an intramolecular hydrogen bonding with the carbonyl group.

Molecular complexes of N-substituted anilines with dichloro-dicyanobezoquinone would be of one type only due to the absence of an acidic centre on the acceptor molecule. The C=O bands at 1695-1678 cm^{-1} in the spectrum of the free acceptor are shifted to lower wavenumbers due to the intermolecular C.T. interaction between the two rings of the molecules forming the complex. The $\pi-\pi^*$ interaction reflects itself in the shift of the γ_{OH} bands of the donor molecules to higher wavenumbers.

The C≡N band shifts to lower values in case of e and f i.e. molecules incapable to participating in the $n-\pi^*$ transition. For a, b, c, g and h the C≡N band appears into two bands in the spectra of the molecular complexes, these are situated at lower and higher wavenumber compared to the band of the free acceptor.

On comparing the behaviour of N-substituted anilines with that of phenyl substituted anilines, it can be pointed out that they are not capable of contributing in $n-\pi^*$ bonding with chloranilic acid. This is due to the high n-ionisation potentials of anilines with acceptor substituents. Anilines with donor substituents which facilitate the $n-\pi^*$ transition form molecular compounds in which the lone pair on the nitrogen atom is blocked by proton transfer from the acceptor molecule.

References

1. W. R. Carper, R. M. Hedges and H. N. Simpson, *J. Phys. Chem.* (Ithaca) 1965, **69**, 1707.
2. S. K. Chakrabarti and S. Basu, *Trans. Faraday Soc.*, 1964, **60**, 465.
3. R. Foster, D. L. Hammik and P. J. Placito, *J. Chem. Soc.*, 1956, 3881.
4. G. Briegleb and J. Czekalla, *Z. Elektrochem.* (*Ber. Bunsengesell physik. Chem.*), 1959, **63**, 6.
5. J. L. Bellamy, "The Infrared Spectra of Complex Molecules", 2nd. Edit. Methuen, London, 1958.
6. R. Mecke, *Z. physik. Chem. Abt.*, (2) 1932, **16**, 409.
7. R. D. Kross and V. A. Fassel, *J. Amer. Chem. Soc.*, 1957, **79**, 38.
8. R. M. Issa and M. M. El-Essawey, *Z. physik. Chem.* (*Leipzig*), 1973, **253**, 96.
9. A. M. Hindawey, A. M. G. Nassar and R. M. Issa, *Acta. Chim. (Akad. Sci. Hungarica)*, 1976, **88**, 341; 1977, **92**, 263; *Egypt. J. Chem.*, 1976, **19**, 257.
10. J. Bellanato, *Spectrochim. Acta*, 1960, **16**, 1344.

Notes

Screening of Metal Complexes for Biological Activity. Part II : Structural and Biological Studies on Iron(II) Oxalate Complexes with Various Nitrogen Donors

S. K. BAJPAI and (Mrs.) P. R. SHUKLA

Department of Chemistry, Lucknow University, Lucknow, India

Manuscript received 21 April 1979, accepted 28 December 1979

THE study of various transition metal complexes as models for understanding the many biochemical processes requiring metal atoms is very much interesting[1,2]. The importance and need for the study of transition metal complexes for their biological significance have been stressed in earlier publications[3,4]. In continuation of the previous work the synthesis of some iron(II) oxalate complexes with ammonia (amm), ethylenediamine (en), aniline (an), *m*-toluidine (*m*-tol), *o*-phenylenediamine (*o*-phdi), 1, 10 - phenanthroline (-phen), *N*-methylpiperazine (*N*-mepz), *N*-phenyl piperazine (*N*-phpz), and some of their structural and pharmacological aspects are described in the present communication.

Experimental

The complexes were prepared by adding excess of amine to a weighed quantity of iron(II) oxalate suspended in ethanol and shaking the reaction mixture for 5-6 hours. The contents were allowed to stand for another six hours and then filtered, washed with dry ether and finally dried in vacuum desiccator over $CaCl_2$. However, ammonia complex could be recovered by addition of acetone using differential solubility method.

Iron was determined gravimetrically as Fe_2O_3. C, H and N were estimated microanalytically. Conductance was measured in formamide at $10^{-3}M$ concentration. IR and diffuse reflectance spectra were recorded on Perkin Elmer 621 and Cary 14 spectrophotometers respectively using nujol discs.

CNS effects and acute toxicity :

Albinomice of either sex (18-22 g) were used to observe the gross effects and effects on central nervous system (CNS)[5]. For LD_{50} (the dose level which kills almost 50% of the experimental population) which is customary yard stick of acute toxicity, the test compounds were given intraperitonially (ip) to the groups of 5 albinomice. They were kept at room temperature of 24±2° and observed continuously for 2 hours and then at two hourly intervals for the next 6 hours. Mortality of the mice during the next 24 hours was recorded and approximate LD_{50} was estimated.

Anti-inflammatory activity (AIA) :

This test was done on mice at the oral dose of $1/5LD_{50}$ according to the technique of Dhawan and Srimal[6].

Diuretic activity (DA) :

Diuretic effects of the compounds were studied in male albino rats weighing between 200-250g at 1/4 LD_{50} dose[7]. Chlorothiazide (100 mg/kg, ip) served as the standard for comparison.

Cardiovascular effects (CVS) :

Adult cats (25-40 kg) of either sex, anaesthetized with pentabarbitone sodium (35 mg/kg iv) were employed. The trachea was cannulated and connected to Marey's tambour. One of the common carotid arteries was also cannulated and connected to a mercury manometer. Records were made on a slow moving Kymograph. The drug was administered through a cannulated femoral vein and the effect on blood pressure was studied on the normal blood pressure level and also on pressure response to adrenaline (0.5-1 μg/kg) and depressor responses to acetylcholin and histamine (both 0.25-0.5μg/kg).

Analgesic activity (AA) :

The analgesic activity was tested by Haffner's Tail Clip method[8]. In this method the mechanical pain was induced by pressing the tail of male rats (90-110g).

Results and Discussion

Analytical, magnetic and spectral data are listed in Table 1 and the results of biological screening are shown in Table 2.

The complexes have been formulated as $[FeC_2O_4(L)_2]$ where L = amm, en, an, tol, phdi, phen, mepz and phpz. Low conductance values (0.25 – 0.40 mhos) show the non ionic nature of the complexes. Lowering of νNH and positive shifting in mixed C=C, C=N and ring vibrations in the IR spectra of all the complexes clearly indicate the coordination of ligand (L) through nitrogen. The coordination of oxalate through oxygen atoms has been confirmed on the basis of considerable negative shift in C–O and positive shift in C=O bands (Table 1)[9]. Fe–N and Fe–O bands have also been observed in lower region of IR spectra of all the complexes which further substantiate the conclusion drawn earlier.

The effective magnetic moments of compound No. 1, 3, 4, 7 and 8 of Table 1 suggested tetrahedral structure, but a band around 6.8 kK in diffuse reflectance spectra suggested C_{2v} symmetry for these complexes[10]. On the other hand the compound No. 2, 5, 6 of Table 1 exhibited a broad band centred

TABLE 1—ANALYTICAL, MAGNETIC AND SPECTRAL DATA

Compound	Analysis (%) Obs. (Cal.) Fe	C	H	N	Molar conductance (mhos)	IR Spectral bands (cm^{-1}) NH	O=C–O		Fe–O	Fe–N	μ_{eff} (B.M)	Diffuse reflectance band nm. (kK)	Dq (cm^{-1})
1. $[FeC_2O_4(amm)_2]$	31.25 (31.40)	13.50 (13.50)	3.35 (3.37)	15.64 (15.75)	0.30	3245 vs 3180 s	1675 vs	1490s	350m	245m	5.27	260 (38.46) 400 (25.00) 1255 (7.97) 1420 (7.04)	750.5
2. $[FeC_2O_4^-(en)_2]$	21.30 (21.16)	27.18 (27.30)	6.10 (6.06)	21.00 (21.22)	0.35	3262 s 3180 s 3160 s	1695 s	1375s	383m	233m	5·60	240 (41.67) 280 (35.72) 365 (27.39) 494 (20.24) 537 (18.62) 600 (16.66) 950 (10.53) 1180 (8.47)	950.0
3. $[FeC_2O_4(an)_2]$	17.00 (16.92)	50.86 (50.95)	3.98 (4.25)	8.50 (8.49)	0.25	3320 s 3200 s	1675 s	1405m	350ms	242m	5.12	248 (40.32) 375 (26.67) 1450 (6.90) 1660 (6.02)	646.0
4. $[FeC_2O_4(m\text{-tol})_2]$	15.50 (15.60)	54.00 (53.67)	5.00 (5.03)	7.68 (7.82)	0.25	3349 vs 3280 vs	1690 s	1358s	358m	267m	5.08	220 (45.45) 260 (38.46) 302 (33.11) 1475 (6.78) 1687 (5.93)	635.5
5. $[FeC_2O_4(o\text{-phdi})_2]$	15.35 (15.52)	47.00 (46.71)	4.28 (4.44)	15.38 (15.55)	0.30	3240 s 3160 m	1700 s	1390m	350m	229m	5.53	239 (41.84) 283 (35.34) 367 (27.25) 442 (22.62) 502 (19.92) 967 (10.34)	958 5
6. $[FeC_2O_4(phen)_2]$	11.00 (11.08)	61.82 (61.94)	3.00 (3.17)	10.98 (11.11)	0.40	*1610 1510 m	1710 vs	1380m	340m	230ms	5.42	250 (40.00) 295 (33.90) 370 (27.03) 495 (20.20) 555 (18.02) 960 (10.42) 1240 (8.07)	924.5
7. $[FeC_2O_4(N\text{-mepz})_2]$	16.02 (16.24)	41.76 (41.89)	7.00 (6.98)	16.30 (16.28)	0.35	3250 s 3120 m	1695 s	1390m	358m	298m	5.07	252 (39.68) 340 (29.41) 490 (20.41) 1280 (7.81) 1450 (6.90)	735.5
8. $[FeC_2O_4^-(N\text{-phpz})_2]$	11.[illegible]0 (11.93)	56.[illegible]0 (56.45)	5.88 (5 98)	11.84 (11.96)	0.26	3250 s	1708 s	1392s	367s	287m	5.11	248 (40.32) 280 (35.72) 300 (33.34) 1250 (8.00) 1460 (6.85)	742.5

FeC_2O_4 : c–o (sym) at 1338 cm^{-1}, c=o (asym) at 1640 cm^{-1}

* mixed C=C, C=N and ring stretching vibrations of $[FeC_2O_4(phen)_2]$

around 10.5 kK with a shoulder around 8.00 kK and are believed to belong to O_h symmetry with slight distortion[11]. A very strong and broad band at 20 kK has been assigned to be a charge transfer band arising from metal to ligand ($t_{2g} \rightarrow \pi^*$) charge transfer. The values of μ_{eff} are in consonance with octahedral geometry assigned to these complexes.

All the complexes under investigation stimulated central nervous system. The increased spontaneous motor activity (SMA) and reactivity were due to direct action of the given compound on the effector cells whereas the increased rate of respiration was a result of dilation of bronchioles and direct stimulation of respiratory centre. Tremor, gasping, piloerection and

TABLE 2—RESULTS OF BIOLOGICAL SCREENING

Compound	Approximate LD_{50} mg/kg ip)	CNS activity at 1/5 LD_{50}	Effects on CVS (Cat) at 2.5 mg/kg I. V.	A. I. A. % inhibition	D. A. at 1/4 LD_{50} (%)	A. A. at 1/5 LD_{50}
$[FeC_2O_4(amm)_2]$	300	Nil	Nil	Nil	40	Nil
$[FeC_2O_4(en)_2]$	800	Increased SMA reactivity and resp.	Hypotension 36 mm Hg for 15 mts.	Nil	46	Nil
$[FeC_2O_4(an)_2]$	300	Increased SMA reactivity and resp., ataxia, tremor and gasping	Hypotension 20 mm Hg for 10 mts.	26	30	Nil
$[FeC_2O_4(m\text{-tol})_2]$	> 1000	Increased SMA reactivity	Hypotension 40 mm Hg for 30 mts	24	32	Nil
$[FeC_2O_4(o\text{-phdi})_2]$	200	Increased SMA reactivity and resp., dragging, tremor	Hypotension 15 mm Hg to 15 mts	18	20	Nil
$[FeC_2O_4(phen)_2]$	300	Increased SMA. reactivity and resp.	Hypotension 32 mm Hg for 20 mts.	6	Nil	Nil
$[FeC_2O_4\ (N\text{-mepz})_2]$	300	-do-	Hypotension 20 mm Hg for 15 mts.	38	Nil	Nil
$[FeC_2O_4N(\text{-phpz})_2]$	300	Increased SMA, reactivity and tremor, piloerection and stranbtail	Hypotension 40 mm Hg for 10 mts	Nil	Nil	Present

Resp.—Respiration, mts—minutes, i. v.—intravenously, i. p.—intraperitonially, SMA-spontaneous motoractivity.

straub-tail etc. produced in some cases were probably due to pronounced toxicity of test compounds. However, the ammonia complex showed no effect on CNS.

Many complexes of this series exhibited weak anti-inflammatory and diuretic activity except ammonia and ethylenediamine complexes which showed considerable diuretic activity. None of the complexes except $[FeC_2O_4\ (N\text{-phpz})_2]$ possessed analgesic property. However, all the complexes except $[Fe\ C_2O_4\ (amm)_2]$ produced hypotension ranging from 15-40 mm of mercury for a short duration.

No definite structure-activity relationship could be established because of irregular trend of pharmacological properties of the complexes. However, toxicity of Fe C_2O_4 $2H_2O$ (LD_{50}=150mg/kg i. p.) has been found to be reduced considerably on coordination and as a matter of fact the $[Fe\ C_2O_4\ (en)_2]$ is not toxic at all. $[Fe\ C_2O_4(N\text{-phpz})_2]$ and $[Fe\ C_2O_4\ (amm)_2]$ have been reported to possess pronounced antipassive cutaneous anaphylactic activity in mice[4].

Acknowledgement

Authors are grateful to Prof. B. N. Dhawan, Scientist in charge, Division of Pharmacology and Therapeutics, Central Drug Research Institute, Lucknow for screening and fruitful discussion.

References

1. B. BRESLOW, in "Metal Ions in Biological Systems" Vol. 2, Marcel Dekker, New York, 1974.
2. C. VENEZIALE, P. WALTER, N. KNEER and H. LARDY, *Biochem.*, 1967, 6, 2129.
3. S. K. BAJPAI and P. R. SHUKLA, *Ind. J. Pharm.*, 1975, 7, 21.
4. S. K. BAJPAI, K. KAR and B. N. DHAWAN, *Curr. Sci.*, 1978, 47, 406.
5. B. N. DHAWAN, M. L.DHAR, M.M. DHAR, B.N. MEHROTRA and C. RAY, *Ind. J. Exptl. Biol.*, 1968, 6, 232.
6. B. N. DHAWAN and R. C. SRIMAL, *Ind. J. Pharm.*, 1971, 3, 4.
7. E. J. BELAIR, A. R. BORRELLI and J. YELMOSKI, *Proc. Soc. Exptl. Biol. Med.*, 1969, 131, 327.
8. F. HAFFNER, *Dtsch. Med. Wochenschr.*, 1929, 55, 731.
9. N. F. CURTIS, *J. Chem. Soc.*, 1963, 4109.
10. C. D. BURBIDGE and D. M. L. GOODGAME, *J. Chem. Soc.*, A. 1967, 694.
11. ABP LEVER, in "Inorganic Electronic Spectroscopy" Elsevier, New York, 1968, 299.

Complexation Reaction of Metal Ions with Peptide Systems. Part (V).

The Stability Constants and Thermodynamic Functions of La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+} and Sm^{3+} with Glycyl-DL-Valine

RANJIT SINGH SANDHU and RANJIT KUMAR KALIA

Chemistry Department, Guru Nanak Dev University, Amritsar, (India)

Manuscript received 25 January 1979, revised 24 September 1979, accepted 25 December 1979

METAL complexes of amino acids and peptides are of theoretical and practical significance. The complexation reactions of number of dipeptides with copper and nickel have been reported in literature[1-7], but no work appears to have been reported with lanthanums. This paper deals with the study of complexes of La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+} and Sm^{3+} with glycyl-DL-valine.

Bjerrum Calvin[8-9] *p*H titration technique as modified by Irving-Rossotti[10] has been employed. Most of peptides are in their zwitter form upto *p*H 6. One equivalent of OH^- is required to titrate the proton from terminal NH_3^+ group between *p*H 7 to *p*H 9. However, in the presence of metal ion the NH_3^+ is titrated at lower *p*H because the metal ion competes with H^+ ion[11].

Experimental

The metal nitrates used were of B. D. H. AnalaR quality. The ligand was obtained from Koch-Light Laboratories Ltd., London. All solutions were prepared in doubly distilled carbon dioxide free water. The metal nitrate solutions were standardised by EDTA method. A fresh ligand solution (0.025*M*) was prepared just before use. Potassium nitrate (1.0*M*) solution was used to maintain constant ionic strength of 0.15*M*. The *p*H was measured on a photovolt digicord *p*H meter having a sensitivity of ±0.002. The *p*H meter was calibrated by suitable buffers. All titrations were carried out in a thermostated bath maintained at temperatures 20 ± 0.1°, 30 ± 0.1° and 40±0.1°. The following sets of solutions were titrated against a standard solution (0.051*M*) carbonate free potassium hydroxide.

A) Acid titration : Nitric acid (0.005*M*, 5ml)

B) Reagent titration : Nitric acid (0.005*M*, 5ml) + reagent (0.025*M*, 5ml)

C) Metal titration : Nitric acid (0.005*M*, 5 ml) + reagent (0.025*M*, 5ml) + metal nitrate (0.005*M*, 5 ml)

In all titrations, the total volume of solution was kept to 50 ml and required amount of potassium nitrate solution (1.0*M*) was added to bring the ionic background to required level. Nitrogen gas was bubbled through the solution to provide an inert atmosphere. The concentrations were corrected for the changes in volume produced by the addition of alkali during titration.

Results and Discussion

$\bar{n}_H$, $\bar{n}$ and pL were calculated by employing the relationships derived by Irving and Rossotti[10]. The practical proton-ligand stability constant (pk_1^H) and the metal-ligand stability constants ($\log K_1$) have been obtained by the Bjerrum half integral method and also graphical methods[10]. The results are shown in Table 1.

The values of $\bar{n}$ obtained are of the order of one indicating the formation of 1 : 1 complexes of La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+} and Sm^{3+} below the *p*H range at which precipitation occurred. The data in Table 1 show an increase in the value of $\log K_1$ with increase in temperature.

TABLE 1—PROTONATION CONSTANT OF THE LIGAND, METAL-LIGAND STABILITY CONSTANTS OF THE COMPLEXES AND THERMODYNAMIC PARAMETERS AT THREE TEMPERATURES

Metal Ions	Protonation constants/metal ligand stability constants	Temperature 20°C	30°C	40°C	ΔG(K cal. mole⁻¹) 20°C	30°C	40°C	ΔH(K cal. mole⁻¹) 30°C	ΔS(cal. mole⁻¹ – deg⁻¹) 30°C
	log pk_1^H	8.47	8.27	8.05					
La^{3+}	log k_1	3.58	3.60	3.64	4.84	5.01	5.24	1.092	20.1
Ce^{3+}	log k_1	3.59	3.62	3.66	4.84	5.06	5.27	1.486	21.6
Pr^{3+}	log k_1	3.59	3.70	3.80	4.84	5.16	5.47	4.433	31.7
Nd^{3+}	log k_1	3.66	3.76	3.93	4.93	5.24	5.68	5.757	36.3
Sm^{3+}	log k_1	3.83	3.91	4.02	5.16	5.45	5.79	4.038	31.3

The order of stability constant at 20° has been observed to be $Sm^{3+} > Nd^{3+} > Pr^{3+} \simeq Ce^{3+} \simeq La^{3+}$. A better separation of log K_1 values amongst Pr^{3+}, Ce^{3+} and La^{3+} has been observed at 30° and 40° where it follows the order $Sm^{3+} > Nd^{3+} > Pr^{3+} > Ce^{3+} > La^{3+}$.

The values of overall changes in free energy ($\triangle G$), enthalpy ($\triangle H$) and entropy ($\triangle S$) have been determined by using the temperature coefficient and Gibbs-Helmholtz equation. These are summarised in Table 1. The value of free energies of formation becomes more negative with increase in temperature. This shows that the complex formation process is spontaneous and the spontaneity increases with increase in temperature. The formation of all the complexes is an endothermic process and it explains the increase in the values of constants with rise in temperature. The complex formation is favoured by the increase in the entropy of the system. It is indicated by the positive values $\triangle S$ in all the cases. The low values of formation constants, free energy of formation, and enthalpy changes shows that these metals have less tendency to form complexes with glycyl-DL-valine.

References

1. G.B. Pettit and D. Leslie, *J. Chem. Soc., Dalton-Trans.* 1975, 20, 2106.
2. M. K. Kim and A. E. Martell, *J. Amer. Chem. Soc.*, 1966, 88, 914 and 1967, 89, 5138.
3. W. L. Koltun, M. Fried and Frank R. N. Gurd, *J. Amer. Chem. Soc.*, 1960, 82, 233.
4. N. V. Petrov, A. P. Boisova and I. A. Savich, *Dokl. Akad. Nank SSSR*, 1970, 192, 574.
5. A. P. Borisova, Yu. V. Granovsic, I. A. Savich and V. I. Spitsyn, *Vestrl. Mosk. Univ. Ser. II*, 1967, 22, 41.
6. A. P. Brunetti, J. Burke, M. C. Lim and G. H. Nancollas, *J. Solution Chem.*, 1972, 1, 153.
7. D.R. Williams, *J. Chem. Soc., Dalton Trans.*, 1976,1012 and 1068.
8. M. Calvin and K. W. Wilson, *J. Amer. Chem. Soc.*, 1945, 67, 2003.
9. J. Bjerrum, Metal amine formation in aqueous solution, Kopenhagen, P. Hasse and Son, 1941, 298.
10. H. Irving and H. S. Rossotti, *J. Chem. Soc.*, 1953, 3397 and 1954, 2904.
11. Gunther L. Eichhorn, Inorganic Biochemistry, Vol. I, P. 134. Elsevier Scientific Publishing Company, New York.
12. L. G. Sillen and A. E. Martell, Stability constants of metal ions complexes. The Chemical Society (London), Special Publication No. 25, 1971.

Rh(III) and Ru(III) Complexes of the Ligand 1-Imino-3-Thioisoindoline

A. K. NIGAM*

Department of Chemistry, D.B.S. College, Dehradun

and

G. D. TIWARI

Department of Chemistry, V. S. S. D. College, Kanpur

Manuscript received 7 April 1979, accepted 28 December 1979

THE ligand 1-Imino-3-Thioisoindoline has recently been used for the gravimetric determination of a number of metal ions by the authors[1-7]. The present investigation deals with the Rh(III) and Ru(III) complexes of the ligand. Investigations have indicated that the ligand reacts with these metals at *p*H ranging from 7.5 to 10.0 giving precipitate of insoluble metal complexes.

All the reagents used were of AnalaR grade. The ligand was prepared by the method of Baguley and Elvidge[8].

The following stock solutions were prepared.

1. 1-Imino-3-Thioisoindoline about 0.1% sodium salt solution of the ligand in NaOH.
2. $RhCl_3 \cdot 3H_2O$ (Johnson-Matthey Co.). A 0.25 W/V solution of hydrated salt in water.
3. $RuCl_3 \times H_2O$, as above.

Preparation of Complexes :

A freshly filtered soln. of the ligand was added in excess to soln. No. 1. A yellow brown ppt. of rhodium complex was obtained. It was digested on a water bath for 10 minutes and then filtered, washed with water for several times and then with alcohol, dried at 70 to 105° in an air oven.

In the case of ruthenium(III) a black ppt. was obtained under similar conditions.

Results and Discussion

The analytical data indicates the metal to ligand ratio as 1:3. Both the complexes were found to be diamagnetic. The infrared spectra of the complexes and the ligand were examined to establish the exact structure of the complexes. The infrared spectra indicates the presence of γ(M-N) and γ(M-S) bonds in both the complexes. Coordination of thiocarbonyl sulphur to the metal ion is also clearly indicated ; it also indicates the absence of N-H bond in the two complexes. Thus it may easily be concluded that the Rh and Ru ion in the

*Address for correspondence.

complexes are coordinated through both thiocarbonyl sulphur and the nitrogen atom of the ligand. This indicates that Rh and Ru form an inner complex type structure. The reflectance spectra of the complexes was also examined. Both the complexes were found to be insoluble in water and most of the organic solvents. Thus on the basis of analytical, infrared, magnetic moment and reflectance data octahedral configuration have been proposed for the rhodium and ruthenium (III) complexes.

Acknowledgement

Authors thanks are due to Prof. B. B. Raizada, Head, Deptt. of Chem., D. B. S. College, Dehradun for the interest shown by him in the work and to Dr. R.M. Singh, Principal of the College for providing the necessary facilities.

References

1. A. K. Nigam and G. D. Tiwari, *Indian J. Appl. Chem.*, 1972, 35, 150.
2. A. K. Nigam and G. D. Tiwari, *Science and Culture*, 1973, 39, 345.
3. A. K. Nigam and G. D. Tiwari, *J. Indian Chem. Soc.*, 1973, 50, 158.
4. A. K. Nigam and G. D. Tiwari, *J. Indian Chem. Soc.*, 1973, 50, 227.
5. A. K. Nigam and G. D. Tiwari, *J. Indian Chem. Soo.*, 1974, 51, 912.
6. A. K. Nigam and G. D. Tiwari, Labdev *J. Sci. Tech.*, 1973, 11-A, 44.
7. A. K. Nigam and G. D. Tiwari, *Science and Culture*, 1976, 42, 265.
8. M. B. Bagoley and J. A. Elvidge, *J. Chem. Soc.*, 1957, 709.

Thiomalate Complexes of Some Divalent Metal Ions

NIRADA KUMARI MOHANTY

Department of Chemistry, Ispat College, Rourkela

and

R. K. PATNAIK

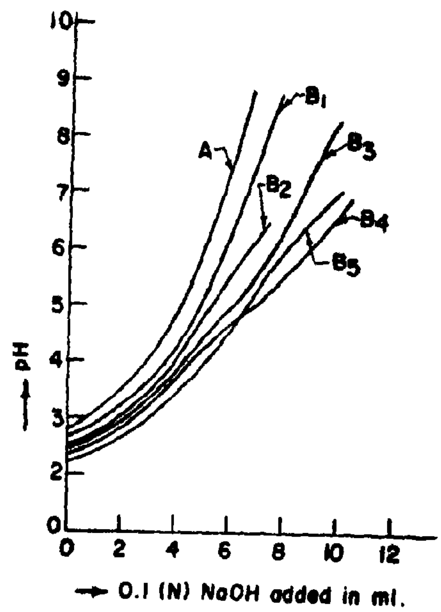
Department of Chemistry, Regional Engineering College, Rourkela-8, (Orissa)

Manuscript received 12 September 1979, accepted 30 November 1979

IN continuation of our earlier work[1] on thiomalate complexes of La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy (III) and Ho(III), we report in this paper the results of our studies on the interaction of Be(II), Mn(II), Co(II), Ni(II) and Zn(II) with thiomalic acid by *p*H titration method.

Experimental

The chemicals used in the investigations were of AnalaR grade. The metals were estimated gravimetrically from their respective salt solutions by standard methods. Ionic strength of 0.1 *M* was maintained by the addition of suitable quantity of $NaClO_4$ to the solutions. All experiments were carried out under nitrogen atmosphere using a Marconi *p*H meter. *p*H titration of 50 ml of solutions containing metal salt and thiomalic acid in different proportions against 0.1 *M* NaOH were performed at 31°±0.5°.



*p*H titration of 50 ml of solutions containing 0.005 gm moles of $NaClO_4$ and

A —3.125×10^{-4} gm. moles of thiomalic acid

B_1—3.125×10^{-4} gm. moles of thiomalic acid and 2.5×10^{-4} gm. moles of $MnSO_4$

B_2—3.125×10^{-4} gm. moles of thiomalic acid + 2.5×10^{-4} gm. moles of $Co(ClO_4)_2$

B_3—3.125×10^{-4} gm. moles of thiomalic acid + 2.5×10^{-4} gm. moles of $NiSO_4$

B_4—3.125×10^{-4} gm. moles of thiomalic acid + 2.5×10^{-4} gm. moles of $ZnSO_4$

B_5—3.125×10^{-4} gm. moles of thiomalic acid + 2.5×10^{-4} gm. moles of $Be(ClO_4)_2$

against 0.1 *M* sodium hydroxide.

Results and Discussion

The amount of acid liberated during complex formation between M^{2+} ions (where M=Be, Mn, Co, Ni and Zn) and thiomalic acid, remains the same even if the metal to ligand ratio is increased from 1 : 1.25 to 1 : 5 which indicates the formation of 1 : 1 type of complex. The reaction taking place due to the interaction of these divalent metal ions with thiomalic acid can be represented as

$$M^{2+}+H_3TML \rightleftharpoons C+nH^+ \quad \ldots (1)$$

$$\text{Hence, } K=\frac{[C]\,[H^+]^n}{[M^{2+}]\,[H_3TML]} \quad \ldots (2)$$

It can be shown as in the citrate complex of cadmium[2]

and yttrium[3] and malate complex of yttrium[4] that,

$$\frac{\triangle[NaOH] - a/b\triangle[TTML]}{[C]} = n - a/b \quad \ldots (3)$$

Where, $a = \frac{k_1}{[H^+]} + 2\frac{k_1 k_2}{[H^+]^2} + 3\frac{k_1.k_2.k_3}{[H^+]^3}$

and $b = 1 + \frac{k_1}{[H^+]} + \frac{k_1.k_2}{[H^+]^2} + \frac{k_1.k_2.k_3}{[H^+]^3}$

$\triangle[NaOH] = [NaOH]_B - [NaOH]_A$; $\triangle[TTML] = [TTML]_B - [TTML]_A$ $[NaOH]_A$, $[NaOH]_B$, $[TTML]_A$, $[TTML]_B$, [C] and n are represented by molar concentrations of sodium hydroxide at Curve A and B, total thiomalate concentration at Curve A and B, thiomalate complex and the number of protons liberated per gm. atom of metal ion respectively. k_1 (2.291×10^{-4}), $k_2(2.291\times10^{-5})$ and $k_3(4.266\times10^{-11})$ are the first, second and third dissociation constants[5] of thiomalic acid respectively.

When the formation of the complex is complete, [C]=[Metal Salt]

$$\text{Hence} \frac{\triangle[NaOH]-a/b\triangle[TTML]}{[\text{Metal Salt}]} = n - a/b \quad \ldots (4)$$

The values of $\triangle$[NaOH], $-\triangle$[TTML], [Metal salt] and then n were calculated at different *p*H values by the methods adopted earlier. The values of n are found to be less than 2 below *p*H 4.6, 5.8, 5.0, 4.8 and 4.6 for beryllium, manganese, cobalt, nickel and zinc respectively. Hence below these *p*H values a neutral complex C is formed in each case with liberation of two protons according to the equation

$$M^{2+} + H_2TML \rightleftharpoons C + 2H^+$$

The concentration of complex C was calculated below these *p*H values by assuming n values to be 2, by the equation (4) and K values were calculated as before by the equation (2). The mean values of $-\log K$ are found to be 5.17 ± 0.11, 5.91 ± 0.05, 5.84 ± 0.09, 5.48 ± 0.11 and 4.28 ± 0.16 for beryllium, manganese, cobalt, nickel and zinc thiomalate system respectively. The values of n are greater than 2 and less than 3 at and above *p*H 4.6, 5.8, 4.8 and 4.6 for beryllium, manganese, nickel and zinc respectively. Hence this indicates the dissociation of the neutral complex C, according to the equation (5)

$$C \rightleftharpoons C_1^- + H^+ \quad \ldots (5)$$

The equilibrium constant K_1 can be represented by the equation (6)

$$K_1 = \frac{[C_1^-][H^+]}{[C]} \quad \ldots (6)$$

It can be shown as in the case of cadmium citrate complex[8] that

$$K_1 = \frac{(n-2)[H^+]}{(3-n)} \quad \ldots (7)$$

The values of K_1 are calculated by equation (7) and the mean values of $-\log K_1$ are found to be 4.82 ± 0.15, 7.48 ± 0.24, 5.38 ± 0.15 and 5.10 ± 0.06 for beryllium, manganese, nickel and zinc respectively.

The results indicate that the stabilities of the thiomalate complexes of divalent metal ions studied in the present investigation decrease in the order $Zn^{2+} > Be^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+}$ which is in agreement with the observations[4-7] made by earlier workers.

Acknowledgement

Thanks are due to the Ministry of Education, Govt. of India for the award of Research Training Scholarship to one of us (N.K.M) and for a research grant.

References

1. N. K. Mohanty and R. K. Patnaik, *J. Indian Chem. Soc.*, (Communicated)
2. R. K. Patnaik and S. Pani, *J. Indian Chem. Soc.*, 1957, 34, 673.
3. K. K. Tripathy and R. K. Patnaik, *Acta. Chim. Hung.*, 1973, 79, 279.
4. N. K. Mohanty and R. K. Patnaik, *J. Indian Chem. Soc.*, 1976, 53, 337.
5. G. R. Lenz and A. E. Martell, *Inorg. Chem.*, 1965, 4, 378.
6. G E. Cheney, Q. Fernando and H. Freiser, *J. Phys. Chem.*, 1959, 63, 2055.
7. W. Manch and W. C. Fernelius, *J. Chem. Educ.*, 1961, 38, 192.
8. W. Stricks, I. M. Kolthoff and A. Heyndrick, *J. Amer. Chem. Soc.*, 1954, 76, 1515.

Some Anionic Complexes of Organometal (III) Derivatives

T. N. SRIVASTAVA and (Mrs.) KIRAN SINGHAL

Chemistry Department, Lucknow University, Lucknow-226 007, India

Manuscript received 14 June 1979, accepted 30 November 1979

A few physico-chemical studies such as electrophoresis anion exchange, paper chromatography have been reported [1,2] to indicate complexation between organothallium(III) cations and tetraalkyl-ammonium salts. Some organothallium complexes of the general formula $[R_4N][PhTlX_3]$ and $[R_4N][PhTlX_4]$ have also been isolated in the solid state[3]. Corresponding anions of organometal(III) containing mixed halo-and halo-pseudohalo are not known. This investigation for the first time reports the synthesis and characterisation of such anionic complexes of the formula $[R_4N][R'_2MXX']$ (R=Me, Et, Bu ; R'=Ph or Bu ; X and X' = Cl, Br, I, N_3 or NCSe).

Experimental

Organometal(III) derivatives R_2MX (R = Bu or Ph ; X = Cl, N_3 or NCSe ; M = Ga, In or Tl) were prepared by the reported methods[4,5].

The new solid organometal(III) complexes have been prepared by the direct interaction of tetraalkylammonium salts with di-organometal(III) compounds.

In a typical experiment, 2.1 g (1 m mole) of tetramethylammonium iodide was dissolved in anhydrous methanol (20 ml) and added dropwise to a stirring suspension of dibutylindium azide (2.7 g, 1 m mole) in methanol (20 ml). The mixture was refluxed for about 6 hrs and filtered. The filtrate on concentration yielded pale yellow tetramethylammonium dibutylindium azide iodide which was recrystallised from the same solvent (m.p. 136°). Other complexes were similarly isolated and are listed in Table 1.

TABLE 1—ANALYTICAL DATA OF DI-ORGANOMETAL (III) MIXED HALO- AND HALO-PSEUDOHALO-ANIONS

Compounds	M. P.	Analysis % Found (Cal.)		
		M	C	H
$[Me_4N][Ph_2GaClBr]$	198	17.12 (17.92)	48.21 (47.92)	5.53 (5.49)
$[Bu_4N][Ph_2GaClBr]$	192	12.36 (12.18)	57.82 (57.68)	7.51 (7.89)
$[Et_4N][Ph_2GaClBr]$	>240	15.47 (14.87)	51.11 (51.00)	6.31 (6.37)
$[Me_4N][Bu_2GaSeCNI]$	>240	14.20 (14.28)	29.41 (29.38)	6.30 (6.12)
$[Me_4N][Bu_2InClI]$	112	25.13 (24.48)	31.01 (30.93)	6.48 (6.44)
$[Me_4N][Bu_2InSeCNI]$	>240	21.71 (21.53)	29.81 (21.21)	5.70 (5.61)
$[Me_4N][Bu_2InN_3I]$	136	25.12 (24.36)	30.82 (30.50)	6.38 (6.35)
$[Et_4N][Bu_2InN_3I]$	>260	22.44 (21.78)	40.96 (40.90)	7.21 (7.19)
$[Et_4N][Ph_2TlClBr]$	164	34.37 (33.80	39.87 (39.76)	5.01 (4.97)
$[Bu_4N][Ph_2TlClBr]$	>240	28.67 (28.51)	46.82 (46.96)	6.51 (6.42)
$[Me_4N][Ph_2TlClI]$	240d	35.02 (34.31)	32.38 (32.29)	3.76 (3.70)
$[Me_4N][Bu_2TlN_3I]$	230d	36.86 (36.36)	25.71 (25.66)	5.51 (5.34)

The products are crystalline solids. They are sparingly soluble in common organic solvents but dissolve in methanol or nitrobenzene. The molar conductance (24-29 ohm^{-1} cm^2 $mole^{-1}$) in nitrobenzene corresponds to 1 : 1 electrolyte.

Results and Discussion

Vibrational frequencies associated with the cations are in close agreement to those reported[6] and are not tabulated. Absorptions associated with the various modes of vibration of pseudohalide groups have been identified. Three absorptions associated with νNCSe, νC-Se and δ NCSe appear at 2050 cm^{-1}, 660 cm^{-1} and $\sim$400 cm^{-1} indicating the presence of N-bonded selenocyanate group. Anions containing the azido group also give rise to three absorptions $\sim$2050 cm^{-1}, $\sim$1340 cm^{-1} and $\sim$665 cm^{-1} attributed to asymmetric, symmetric stretchings and bending mode of the covalently bonded, linear $N=\overset{+}{N}=\overset{-}{N}$ group. In the far infrared region absorptions due to Ga - C, In - C and Tl - C have been identified at 600 cm^{-1}, 580 cm^{-1} and 570 cm^{-1} respectively which are in good agreement with the reported values[7-9]. Metal-halogen and metal-nitrogen absorptions lie beyond the recorded range of the spectra.

The complex anions are therefore ionic in character and on the basis of analytical data, may be formulated as $[R_4N]$ $[R'_2MXX']$, containing tetracoordinated metal atom.

Acknowledgement

Thanks are due to State Council of Science and Technology for financial assistance.

References

1. G. FARAGLIA, A. CASSOL and R. BARBIERI, Proc. Journ'ees Helle'nes de Se'paration Imme'diate et de Chromatographie (III J. I. S. I. C.) Ass. Greek Chem. Ed., Athens, 1966, 271.
2. G. FARAGLIA, L. RONCUCCI FIORANI, B. L. PEPE and R. BARBIERI, Proc. Autumn Meeting, University of Padova, 1966.
3. G. FARAGLIA, L. RONCUCCI FIORANI, B. L. PEPE and R. BARBIER, *Inorg. Nuclear Chem. Letters*, 1966, 2, 277.
4. T. N. SRIVASTAVA and KIRAN KAPOOR, *Indian J. Chem.*, (in press).
5. A. K. KOCHETKOV and R. KH. FREIDLINA, *Org. Khim*, 1950, 7, 144.
6. Z. MASLOWSKY, *J. Organometal. Chem.*, 1974, 81, 153.
7. M. WILKINSON and I. J. WORRALL, *J. Organometal. Chem.*, 1975, 93, 39.
8. M. J. S. GYNANE and I. J. WORRALL, *J. Organometal. Chem.*, 1974, 81, 329.
9. MINORU TANAKA, HIDEO KUROSAWA and ROKURO OKAWARA, *Inorg. Nuclear Chem. Letters*, 1967, 3, 565.

Copper(III) as an Oxidative Titrant for Alanine, 2-aminobutyric Acid and Arginine mono hydrochloride

P. K. JAISWAL* and K. KUMAR

Food Research and Standardisation Laboratory, Navyug Market, Ghaziabad-201 001, India

Manuscript received 24 September 1979, accepted 30 November 1979

PREPARATION, standardisation and applications of tellurato cuprate(III) have been described in earlier publications[1-3]. The present communication describes the microdetermination of alanine, 2-aminobutyric acid and arginine monohydrochloride using Cu(III).

It has been found that alanine, 2-aminobutyric acid and arginine monohydrochloride required 20,26 and 56 equivalents of the oxidant respectively for their complete oxidation. The results are reproduciable within ±0.5%. Tellurate does not interfere as oxidant, since Cu(III) being a stronger oxidant, reoxidises any tellurite that may be formed in the reaction mixture. It was also observed that refluxing and cooling of the reaction mixture is essential to complete the oxidation, as determination of Cu(III) immediately after mixing or after allowing to stand for 15 minutes at room temperature gave erroneous results indicating incomplete oxidation.

Experimental

Materials : All the chemicals used were of reagent grade. Telluratocuprate(III) reagent was prepared and standardised as described earlier[1]. Alanine, 2-aminobutyric acid and arginine monohydrochloride were of B.D.H. biochemical grade.

Procedure : An aliquot of the aqueous solution containing 1.0-3.5 μ moles of amino acid was added to an excess of Cu(III) reagent (1.56×10^{-4} μ moles). The mixture was refluxed on a hot plate for 15 minutes, cooled and the unconsumed Cu(III) determined as described earlier[1]. Total volume of solution mixture was kept 20 ml. Blank experiments were also conducted under identical conditions. The results are given in Table 1.

References

1. S. CHANDRA and K. L. YADAVA, *Talanta*, 1968, 15, 349.
2. P. K. JAISWAL and S. CHANDRA, *Chimie Anal.*, 1969, 51, 493.
3. P. K. JAISWAL, *Microchem. J.*, 1970, 15, 434.

*To whom correspondence may be addressed : at Directorate of Marketing and Inspection, New Secretariat Building, Nagpur-440 001.

TABLE 1—OXIDATION OF ALANINE, 2-AMINOBUTYRIC ACID AND ARGININE MONOHYDROCHLORIDE USING TELLURATO COPPER (III) REAGENT

Amino Acid	Amount of amino acid taken μ mole.	Copper (III) consumed equiv./mole of amino acid*			Error %
		a	b	c	
Alanine	2.94	2.42	5.56	19.90	−0.5
2-Aminobutyric acid	2.52	1.64	6.70	25.96	−0.15
Arginine monohydrochloride	1.27	2.52	9.00	55.82	−0.32

* Mean of six results.

(a) Determination of Cu(III) immediately after adding the amino acid solution.

(b) Determination of Cu(III) after allowing the solution mixture to stand for 15 minutes at room temperature.

(c) Determination of Cu(III) after refluxing and cooling the reaction mixture for 15 minutes.

Binary and Ternary Chelates of Sc(III), Y(III) and La(III) with Ethylenediamine tetraacetic Acid as Primary Ligand and Substituted Salicylic Acids as Secondary Ligands

ASHOK KUMAR PANDEY, M. CHANDRA, B. V. AGARWALA and ARUN K. DEY*

Chemical Laboratories, University of Allahabad, Allahabad-211 002

Manuscript received 21 August 1979, accepted 30 November 1979

ETHYLENEDIAMINETETRAACETIC acid (edta) behaves as a polydentate ligand and forms strong complexes with metal ions in solution at low *pH* values[1-4], which remain stable at higher *pH* as well. Thus, edta has widely been used as one of the constituents in the study of a number of ternary complexing systems.

*For correspondence.

The work described here relates to a study of ternary complex formation of several tripositive metal ions viz. Sc(III), Y(III) and La(III) with edta as a primary ligand and 5-chlorosalicylic acid (csa) or 3,5-dibromosalicylic acid (dbsa) as secondary ligands (H_2L) by *p*H-metric titration technique[4-6]. All the experiments were carried out at 25° and ionic strength of 0.1 (KNO_3) in 50% (*v*/*v*) aqueous-ethanol medium.

It may be mentioned here that ternary complexes of these secondary ligands with several bipositive metal ions and 2, 2' bipyridine[7,8], 1,10 phenanthroline[9], and nitrilotriacetic acid[10,11] as primary ligands have earlier been reported from these laboratories.

Experimental

Materials :

Nitrate solutions of Sc(III), Y(III) and La(III), and of NaOH and HNO_3 were prepared using reagent grade chemicals and standardized. Aqueous solutions of KNO_3 and edta, and ethanolic solutions of csa and dbsa were prepared by direct weighing. Redistilled absolute ethanol (BCPW) was used wherever necessary.

Apparatus :

*p*H measurements were made at 25° using expanded scale *p*H meter (Electronic Corpn. of India) with glass-calomel electrode assembly supplied with the instrument.

Procedure :

The *p*H-metric titrations of binary and ternary complexing systems, the composition of the titration mixtures and the calculations were same as described earlier[10].

Results and Discussion

Values of proton ligand stability constants obtained by average value method are recorded in Table 1, which are in agreement with earlier findings[10]. Only 1 : 1 binary metal-chelates of csa and dbsa could be studied. Higher complexing species or hydroxo species likely to be formed after this stage could not be examined due to occurrence of opacity/turbidity/precipitation.

The stability order of metal chelates with respect to various ligands are : dbsa>csa, while those with respect to metal ions are : Sc(III)> Y(III)> La(III).

The values of $\log K^{\text{M-edta}}_{\text{M-edta-L}}$ $\left[K^{\text{M-edta}}_{\text{M-edta}-\text{L}} =\right.$ mixed ligand formation constant in M-edta-L systems] is less than $\log K_1$ [K_1 = first step formation constant of binary complexes with secondary ligands]. During mixed ligand complex formation, the coulombic repulsion between $(\text{M-edta})^{-1}$ species and the incoming ligand L^{2-} lowers the stability of mixed ligand

TABLE 1—EQUILIBRIUM CONSTANTS IN BINARY AND TERNARY COMPLEXING SYSTEM, 25° ; μ=1.0 (KNO_3)

Equilibria	Log equilibrium constants
H_2L(*ligand*)=*csa*	
$H^+ + L^{2-} \rightleftharpoons LH^-$	11.56±0.09
$LH^- + H^+ \rightleftharpoons LH_2$	3.11±0.05
$Sc^{3+} + L^{2-} \rightleftharpoons ScL^+$	9.07±0.03
$Y^{3+} + L^{2-} \rightleftharpoons YL^+$	8.48±0.03
$La^{3+} + L^{2-} \rightleftharpoons LaL^+$	7.75±0.03
$(Sc\ edta)^- + L^{2-} \rightleftharpoons (Sc\ edta\ L)^{3-}$	5.34±0.02
$(Y\ edta)^- + L^{2-} \rightleftharpoons (Y\ edta\ L)^{3-}$	5.08±0.02
$(La\ edta)^- + L^{2-} \rightleftharpoons (La\ edta\ L)^{3-}$	4.88±0.02
$H_2'L$=*dbsa*	
$H^+ + L^{2-} \rightleftharpoons LH^-$	12.05±0.06
$LH^- + H^+ \rightleftharpoons LH_2$	2.86±0.09
$SC^{3+} + L^{2-} \rightleftharpoons ScL^+$	9.68±0.01
$Y^{3+}L^{2-} \rightleftharpoons YL^+$	8.84+0.07
$La^{3+} + L^{2-} \rightleftharpoons LaL^+$	8.20±0.07
$(Sc\ edta)^- + L^{2-} \rightleftharpoons (Sc\ edta\ L)^{3-}$	5.78±0.02
$(Y\ edta)^- + L^{2-} \rightleftharpoons (Y\ edta\ L)^{3-}$	5.57±0.01
$(La\ edta)^- + L^{2-} \rightleftharpoons (La\ edta\ L)^{3-}$	5.38±0.02

complexes. On the other hand formation of ML species, is accompanied by coulombic attraction between M^{3+} and the incoming ligand L^{2-} which justifies $\log K_1 > \log K^{\text{M-edta}}_{\text{M-edta-L}}$. The stability order with respect to metal ions and the ligands follow the same pattern as those in corresponding binary complexing systems.

Acknowledgement

The financial support from Council of Scientific & Industrial Research, New Delhi, is gratefully acknowledged.

References

1. G. SCHWARZENBACH and H. ACKERMAN, *Helv. Chim. Acta*, 1947, 30, 1798.
2. F. F. CARINI and A. E. MARTELL, *J. Amer. Chem. Soc.*, 1957, 75, 4810.
3. G. ANDEREGG, *Helv. Chim. Acta*, 1967, 50, 2333.
4. H. IRVING, R. SHELTON and R. EVANS, *J. Chem. Soc.*, 1958, 3540.
5. M. V. CHIDAMBARAM and P. K. BHATTACHARYA, *J. Inorg. Nuclear Chem.*, 1970, 32, 3271.
6. H. M. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.*, 1953, 3397 ; 1954, 2904.
7. K. Dwivedi, B. K. AGARWAL, M. CHANDRA and A. K. Dey, *J. Indian Chem. Soc.*, 1977, 54, 474.

8. K. Dwivedi, M. Chandra and A. K. Dey, *Transition Metal Chem.*, 1977, 2, 186.

9. B. K. Agrawal, M. Chandra, B. V. Agarwala and A. K. Dey, *Indian J. Chem.*, 1978, 16-A, 340.

10. B. K. Agrawal, M. Chandra, B. V. Agarwala and A. K. Dey, *Indian J. Chem.*, 1977, 15-A, 633.

11. R. K. Mittal, M. Chandra and A. K. Dey, *Monatsh. Chem.*, 1978, 509, 853, 953.

Co(II), Ni(II), Cu(II) and Zn(II) Complexes with 3(2′-furoyl) 2-Cyano Ethyl Crotonate

P. K. PANDA and B. K. MOHAPATRA

Department of Chemistry, Ravenshaw College, Cuttack-753 003, India

Manuscript received 3 November 1979, accepted 20 December 1979

In the programme of preparing complexes of rare and higher co-ordination numbers with divalent first transition series metal ions, polydentate chelating ligands are being synthesised since such ligands dominate the area of higher co-ordination polyhedra in scope, numbers and also from kinetic and thermodynamic stability point of view. Particularly, the compact nature of polydentate schiff's bases make them more effective in attaining high co-ordination structure. Earlier complexation behaviour of bi, tri and tetradentate schiff's bases have been reported[1-5]. In this communication a number of Co(II), Ni(II), Cu(II) and Zn(II) complexes with a bidentate ligand derived from condensation of furfuraldehyde and ethyl cyanoacetate will be presented.

Experimental

Synthesis of the Ligands : Furfuraldehyde and ethyl cyanoacetate in 1:1 proportion were mixed with 1 cc of piperidine as base and refluxed for 6-8 hours. The contents were poured into a 10% solution of hydrochloric acid and kept standing for six days. Pinkish-violet crystalline compound separated out which was filtered, washed with ether and dried in vacuum.

Preparation of Complexes : Ethanolic solution of different metal salts were treated with ethanolic solution of the ligand in 1:2 proportion and the resulting solution refluxed for one hour. On keeping the resulting solution overnight crystalline compounds separated. These were filtered under suction, washed with ethanol and ether and dried in vacuum desiccator.

Metal and nitrogen in the complexes were estimated by standard methods. Conductance was measured in M/1000 acetone solution using Toshniwal conductivity bridge. Magnetic susceptibility measurements were made on solid specimens at room temperature by the Guoy method. I. R. spectra were recorded using Perkin-Elmer-337 and Beckman I. R.-12 spectrophotometers. Electronic spectra were recorded on a Hilger-watt uvispeck spectrophotometer with M/100 chloroform solution of the complexes. Analytical, conductance, magnetic susceptibility and spectral data are recorded in Table 1.

TABLE 1—ANALYTICAL AND SPECTRAL DATA OF COMPLEXES

Compounds	M. P. (°C)	Λ_M (mhos. cm²)	μ_{eff} (B M.)	% metal Found.	% metal Calcd.	% nitrogen Found	% nitrogen Calcd.	Electronic spectra ν_{max} in k. k. (ε)
$CoCl_2L_2$	165	6.5	4.9	11.25	11.51	5.22	5.47	18.8 (35), 8.0 (16)
$CoBr_2L_2$	185	7.3	5.0	9.48	9.82	4.25	4.66	19.2 (38), 8.0 (16)
$Co(NO_3)_2L_2$	180	6.8	5.2	10.15	10.43	9.58	9.91	19.4 (40), 8.2 (18)
$NiCl_2L$	202	7.4	—	18.11	18.30	4.02	4.36	16.5 (50)
$NiBr_2L$	198	8.2	—	14.15	14.37	3.05	3.42	17.4 (54)
$Ni(NO_3)_2L$	176	8.5	—	15.46	15.71	10.91	11.24	18.0 (55)
$CuCl_2L_2$	205	5.8	1.78	12.05	12.30	5.22	5.42	14.8 (30)
$CuBr_2L_2$	196	6.2	1.80	10.21	10.51	4.31	4.63	15.0 (35)
$Cu(NO_3)_2L_2$	190	6.5	1.82	10.85	11.15	9.56	9.83	15.3 (40)
$ZnCl_2L_2$	185	8.2	—	12.26	12.61	5.20	5.40	—
$ZnBr_2L_2$	176	8.4	—	10.45	10.78	4.28	4.62	—
$Zn(NO_3)_2L_2$	183	7.5	—	11.21	11.44	9.56	9.80	—

L=3 (2′—Furoyl)-2-cyano ethyl crotonate.

Results and Discussion

All the complexes have the general formula ML_2X_2 where M = Co(II), Cu(II), Zn(II), X = Cl^-, Br^-, NO_3^- and L = 3(2'-furoyl)-2-cyano ethyl crotonate, excepting the nickel complexes which have the composition MLX_2. Cobalt complexes are pink, nickel complexes red, copper complexes green in colour and zinc complexes are white. They have relatively low melting points and are soluble in acetone in which medium the low molar conductance values (Table 1) indicate them to be non-electrolytes. Magnetic moment of cobalt complexes are in the range of 4.9-5.2 B.M. suggesting a spin free octahedral configuration. Nickel complexes are dimagnetic and copper complexes have moments in the range of 1.78-1.82 B.M. as expected for the presence of a single unpaired electron.

In the infrared spectra of the ligand ν(C=O) appears[6] at 1690, ν(C=C) at 1620 and ν(C≡N) at 2220 cm^{-1}. On the complexation of the ligand, in the metal complexes ν(C=O) is observed ~1590 – 1600cm^{-1} region, where as the absorption due to ν(C≡N) disappears and a new band is observed around 1490 cm^{-1} which can be assigned as ν(C=N). Hence the ligand coordinates through the oxygen of the (C=O) groups and nitrogen of the nitrile group. This has been further substantiated by observation[7] of ν(M – O) and ν(M – N) ~420 – 450 and 250 – 280 cm^{-1} region respectively. In the spectra of nitrato complexes the difference ($\nabla\nu$) between the position of ν_4 and ν_1 band is ~130 cm^{-1} which indicates[8-10] the presence of unidentate nitrato group.

In the electronic spectra of Co(II) complexes two absorption bands were observed ~18.8 – 19.4 (35 – 40) and 8.0 – 8.2 (16 – 18) k. k. regions assignable[11] to $^4T_{1g} \rightarrow {}^4T_{1g}$ (P) and $^4T_{1g} \rightarrow {}^4T_{2g}$ (F) transitions respectively. On the basis of the position of absorption bands and magnetic moment data a spin-free octahedral configuration is expected for these complexes. All the dimagnetic nickel (II) complexes show one broad absorption band ~ 16 – 18 (50 – 55) k. k. regions, which suggests[12,13] a possible square planar configuration for these complexes. Copper (II) complexes give rise to one broad absorption band ~14 – 15.3 (30 – 40) k. k. regions indicating presumably a distorted octahedral configuration. Even though at least three transitions are expected[14,15] in this case, all the three are very close in energy and often give rise to a single broad band envelope. On the basis of analysis, conductance and infrared spectral data, all the zinc complexes have an octahedral environment around the metal ion.

References

1. B. B. Mohapatra, B. K. Mohapatra and S. Guru, *Acta. Chimica* (Budapest), 1977, **94**, 191.
2. B. B. Mohapatra, B. K. Mohapatra and S. Guru, *J. Inorg. Nuclear Chem.*, 1977, **39**, 2291.
3. B. B. Mohapatra, B. K. Mohapatra and S. Guru, *J. Inog. Nuclear Chem.*, 1978, **40**, 1178.
4. N. C. Mishra, B.K. Mohapatra and S. Guru, *J. Indian Chem. Soc.*, 1978, **55**, 839.
5. C. D. Rao, B. K. Mohapatra and S. Guru, *J. Inorg. Nuclear Chem.* (In Press).
6. R. M. Silverstein and G. C. Bassler, "Spectrometric identification of Organic compounds" John Wiley, New York, 1963.
7. J. R. Ferraro, "Low frequency vibration of inorganic and coordination compounds". Plenum Press. New York, 1971.
8. R. V. Biagetti, W. C. Bottjer and H. M. Haendler, *Inorg. Chem.*, 1966, **5**, 379.
9. N. Logan and W. B. Simpson, *Spectrochim. Acta*, 1965, **21**, 857.
10. A.B.P. Lever, *Inorg. Chem.*, 1965, **4**, 1042.
11. A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam, 1968.
12. B. N. Figgis, "Introduction to ligand fields" Wiley, Eastern, New Delhi, 1976.
13. H. B. Gray and C. J. Ballhausen, *J. Amer Chem. Soc.*, 1963, **85**, 260.
14. C. A. Agambar and K. G. Orrel, *J. Chem. Soc.*, 1969, 897.
15. D. W. Smith, *Inorg. Chem.*, 1966, **5**, 2236.

Mono-organotin (IV) Derivatives of Hydroxamic Acids

C. K. NARULA and V. D. GUPTA*

Chemistry Department, University of Rajasthan, Jaipur-302 004

Manuscript received 23 October 1979, accepted 20 December 1979

ORGANOTIN (IV) derivatives of hydroxamic acids have aroused considerable interest recently[1-4]. However, except a few phenyltin derivatives of N-phenylbenzhydroxamic acid[5], the chemistry of mono-organotin (IV) hydroxamates still remains unexplored. In the present paper we have described the synthetic and some structural aspects of some five-, six-and seven-coordinate mono-organotin (IV) compounds derived from hydroxamic acids.

Experimental

Reagents :

Hydroxamic acids were prepared by the literature procedure[6,7]. Butyltin sesquoxide was purchased from T.N.O. Phenyltin trichloride and phenylstannoic acid were prepared by the reported methods[8]. Phenyltin triisopropoxide was prepared by the reaction of sodium isopropoxide with phenyltintrichloride[9]. Benzene and tetrahydrofuran were dried over sodium wire.

General method of preparation of products (Table 1) :

The reaction of organotin sesquoxide, $RSnO_{1.5}$, with hydroxamic acids, RC(O)NR'OH, (LH) in 1:1, 1:2

*Present Address : Chemistry Department, Faculty of Science, Banaras Hindu University, Varanasi-221 005, India.

and 1:3 molar ratios carried out in benzene gave sharp melting crystalline solids of general formulae $R_2Sn_2O_2L_2$, $(RSnL_2)_2O$ and $RSnL_3$ respectively; water was removed azeotropically with the solvent. Solvent was removed and compounds were dried at reduced pressure. Reactions have been summarized in Table 1.

Preparation of bis-(acetohydroxamato) chlorophenyltin (IV):

Phenyltin trichloride diluted with THF was added dropwise to a cooled suspension of sodium acetohydroxamate (prepared by the reaction of sodium isopropoxide with acetohydroxamic acid) in THF. This was stirred at 25° for 12 hrs. Sodium chloride and unreacted sodium acetohydroxamate were filtered off. Solvent was removed and compound was dried at 25°/.01 mm/2h. Yield 97%, M. P. 190°, (Analysis calculated for $C_{10}H_{13}N_2O_4SnCl$, Sn, 31.3; N, 7.38: Found Sn, 32.4; N, 7.00).

Preparation of tris-(acetohydroxamato) phenyltin(IV):

The title compound separates as a white powder when acetohydroxamic acid was allowed to react with phenyltin triisopropoxide in 3:1 ratio in refluxing THF. The product is filtered and dried at 50°/1mm/1hr. Yield 91%, M.P. 210°, (Analysis calculated for $C_{12}H_{17}N_3O_6Sn$, Sn 28.43, N 10.06; Found Sn 28.74, N 9.98).

Molecular weight measurements (Gallenkamp ebulliometer) of typical samples reveal that all of these exist as unimolecular species.

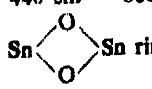
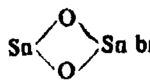
Result and Discussion

In the IR spectra of all these products, νOH present in parent hydroxamic acids at 3050-3080 cm^{-1} is absent. νNH is observed at ~3200 cm^{-1}. Amide I band shifts to 1530-1560 from 1620-1660 cm^{-1} suggesting the

TABLE 1 MONO-ORGANOTIN (IV) DERIVATIVES OF HYDROXAMIC ACIDS

S. No.	Compound	Yield	M. P.	Found Analysis (%) (Calcd.) Sn	N
1.	$[PhC(O)NPhOSnBu(O)]_2$	87	70	30.05 (29.45)	3.48 (3.47)
2.	$[PhC(O)NHOSnBu(O)]_2$	98	205d	36.22 (36.23)	4.25 (4.27)
3.	[PhC(O)N p-tolyl OSnBu(O)]$_2$	98	82	28.25 (28.35)	3.21 (3.34)
4.	$[MeC(O)NHOSn Ph(O)]_2$	97	180	41.57 (41.56)	4.75 (4.90)
5.	$[(PhC(O)NPhO)_2SnBu]_2O$	97	52	19.88 (19.54)	4.42 (4.61)
6.	$[(PHC(O)NHO)_2SnBu]_2O$	97	162	25.98 (26.05)	6.07 (6.14)
7.	[(PhC(O)N p-tolyl O)$_2$SnBu]$_2$O	98	80	18.11 (18.16)	3.29 (3.40)
8.	$[PhC(O)NPhO]_3SnBu$	80	58	15.01 (14.62)	5.11 (5.17)
9.	$[PhC(O)NHO]_3SnBu$	98	138	20.18 (20.38)	6.62 (7.19)
10.	[PhC(O)N p-tolyl O]$_3$SnBu	90	65	13.80 (13.86)	4.74 (4.90)

bidentate nature of the ligand. νN – O appears at ~920 cm^{-1} except in acetohydroxamic acid derivatives where it appears at 930 cm^{-1}. νSn – C bands can be observed at 510 and 610 cm^{-1}[10] in alkyltin (IV) compounds. Characteristic Ph – Sn appears at ~1070cm^{-1}.

In the products $R_2Sn_2L_2O_2$ (Table I, 1-4) the band present in the ligands at 440 cm^{-1} becomes intense suggesting the presence of  ring[10]. Bidentate nature of ligand and presence of  bridge indicate that the compound involves two trigonal bipyramids joined through Sn – O – Sn linkage.

The products $(RSnl_2)_2O$ (Table-I, 5-8) seem to involve two octahedrals with corner joined through Sn – O – Sn linkage. Products $RSnL_3$ (Table-I, 9-10) and tris-(acetohydroxamato) phenyltin(IV) may be examples of seven co-ordinate mono-organotin(IV) derivatives. In the PMR spectra, apart from usual signals, only one methyl signal is observed at 7.5T for methyl of *p*-tolyl in N-*p*-tolyl benzhydroxamic acid derivative. It seems, that either ligand exchange is very fast or methyls of *p*-tolyl group are too far to be affected by the different ligand orientations in the molecule.

Acknowledgement

Authors are thankful to The University Grants Commission, New Delhi, India for financial assistance to one of us (CKN).

References

1. P. G. HARRISON, *Inorg. Chem.*, 1973, **12**, 1545.
2. P. G. HARRISON and T. J. KING, *J. Chem. Soc., Dalton*, 1974, 2298.
3. P. G. HARRISON, T.J. KING and J.A. RICHARDS, *J. Chem. Soc., Dalton*, 1975, 826.
4. P. G. HARRISON, T.J. KING and R.C. PHILLIPS, *J. Chem. Soc., Dalton*, 1976, 2317.
5. B. PRADHAN and A K. GOSH, *J. Organometal. Chem.*, 1977, **131**, 23.
6. A. H. BLATT, "Organic Syntheses", Vol. II, John Wiley, New York, 1950.
7. L. W. JONES and A. W. SCOTT, *J. Amer Chem. Soc.*, 1922, **44**, 407.
8. A.K. SAWYER, "Organotin Compounds, Vol. II, Marcel. Dekker, Inc., New York, 1971.
9. C.K. NARULA and V.D. GUPTA, (Under communication).
10. T. TANAKA, *Organometal. Chem. Rev.*, 1970, **5**, 1.

Synthesis of Ammonium, Sodium and Potassium Salts of Heteropoly Anion $[SbV_{12}O_{36}]^{7-}$

S. K. ROY and P. P. JHA

University Department of Chemistry, Ranchi College, Ranchi-834 008

Manuscript received 22 December 1979, accepted 31 December 1979

THE existence of $[V_{12}O_{36}]^{12-}$ isopoly anion has been established by extensive studies on the formation and structure of phosphoro-12-vanadic heteropoly acids[1,2]. They have established the existence of $[PV_{12}O_{36}]^{7-}$ heteropoly anion, in solution phase. The present communication deals with the synthesis of ammonium, sodium and potassium salts of a new heteropoly anion $[SbV_{12}O_{36}]^{7-}$.

The conditions of formation of these heteropoly salts have been established with the help of *p*H and thermometric titrations in the same manner as discussed in the previous communications[3].

Ammoniumvanadoantimonate—35 ml of .2*M* NH_4VO_3, 15 ml of glacial acetic acid and 50 ml of .013*M* potassiumpyroantimonate, $K[Sb(OH)_6]$, were mixed together (*p*H 3.5) by continuous stirring for half an hour. The mixture was digested for 2 hours under controlled temperature of 80° in a thermostat. It was kept in a steam bath for three hours and then left for a few days. Intense deep brown compound separated after five days. For analysis of the compound vanadium was estimated volumetrically[4] by potassium peramanganate method and colorimetrically[5] by hydrogen peroxide method. Antimony was estimated iodometrically[5] and colorimetrically[6] by rhodamine B method. Nitrogen and hydrogen were estimated by element estimation technique. From analysis : (Found : V,31.450 ; Sb, 6.210 ; N, 5.012 ; H,4.309 per cent. Calcd for $(NH_4)_7$ $[SbV_{12}O_{36}]$ $28H_2O$: V,31.546 ; Sb,6.289 ; N,5.051 ; H,4.324 per cent). The final representation of the formula was according to the views suggested by Spitsyn for complex heteropoly an ion $[X^{n+}V_{12}O_{36}]^{(12-n)-}$.

Sodiumvanadoantimonate— The reddish brown sodium salt of heteropoly anion $[SbV_{12}O_{36}]^{7-}$ was isolated by the same method as adopted for the synthesis of ammonium salt with slight variation in *p*H. Here 25 ml of .2*M* $NaVO_3$ solution, 25 ml of glacial acetic acid and 60 ml of .013 *M* K $[Sb(OH)_6]$ solution were mixed together (*p*H 2.9) and a reddish brown powdery compound was separated after an interval of seven days by following the systematic treatments as discussed earlier. From analysis : (Found : V,34.005 ; Sb,, 6.691 ; Na, 8.901 ; H,1.9 6 per cent. Calcd for Na_7 $[SbV_{12}O_{36}]$ $18H_2O$: V,34.261 ; Sb, 6.796 ; Na,8.969 ; H,2.005 per cent). Sodium was estimated by flame photometric method.

Potassiumvanadoantimonate—Light brown amorphous type compound was separated from a solution

(pH 4.3) of 20 ml of .2M KVO_3, 7 ml of glacial acetic acid and 40 ml of .013M $K[Sb(OH)_6]$ after an interval of twelve days, following the same treatment as has been described for the synthesis of the ammonium salt. From analysis : (Found V, 25.344; Sb, 5.051; K, 11.317; H, 3.798 per cent. Calcd for $K_7[SbV_{12}O_{36}]$ $46H_2O$: V, 25.383; Sb, 5.060; K, 11.323; H, 3.815 per cent. Potassium was estimated by flame photometric method.

Molecular Weight Determination—The molecular weights of all the salts of $[SbV_{12}O_{36}]^{7-}$ heteropoly anion, were successfully determined by the methods as has been done by Alexander[7] and by Thilo and Krüger[8] for the molecular weight determinations of certain inorganic polyacids and polyphosphates etc, in water and molten sodium sulphate decahydrate. This determination showed the molecular weights of the compounds $(NH_4)_7[SbV_{12}O_{36}]$ $28H_2O$, $Na_7[SbV_{12}O_{36}]$ $18H_2O$ and $K_7[SbV_{12}O_{36}]$ $46H_2O$ to be 1905, 1760 and 2375, as compared with the calculated values 1940, 1795 and 2411 respectively, which are in the range of fair agreement.

References

1. A. A. Ivakin and L. D. Kurbatova, *Koord. Khim.*, 1975, 1(11), 1481; 1976, 2(2), 217.
2. L. P. Kazanaskii, V.F. Chuvaev and V. I. Spitsyn, *IVz. Akad. Nauk*, U.S.S.R., 1976, 2, 256.
3. Salil Kumar Roy and G. C. Bhattacharya, *J. Indian Chem. Soc.*, 1976, 53, 1074; 1977, 54, 638.
4. W. W. Scott and N. H. Furman, "Standard Methods of Chemical Analysis", Technical Press Ltd., London, Vol. I, p. 871.
5. A. I. Vogel, "Text Book Quantitative Inorganic Analysis", Longman, Green and Co. Ltd., London, 1960, p. 576, 376.
6. F. D. Snell and C. T. Snell, "Colorimetric Analysis". D. Van Nostrand Company Inc., 1966, Vol. 2, p. 110.
7. G. B. Alexander, *J. Amer. Chem. Soc.*, 1954, 76, 2094; 1953, 75, 2887.
8. B. Thilo and G. Krüger, *Z. Electrochem.*, 1957, 61, 24.

Studies on 3-Bromo-2-Hydroxy-5-Methylacetophenone Oxime (BHMAO) as Metal Complexing Agent : Spectrophotometric Determination of Palladium (II), Copper (II), Nickel (II) and Cobalt (II)

KHEMTI LAL and (Km.) SITA RANI MALHOTRA

Chemistry Department, D. N. College, Meerut-250 002

Manuscript received 29 June 1979, accepted 30 November 1979

IN continuation of our studies on orthophenolic oximes[1,2], the present work reports the use of newly synthesized 3-bromo-2-hydroxy-5-methylacetophenone oxime (BHMAO) for the spectrophotometric determination of microgram quantities of Pd(II), Cu(II), Ni(II) and Co(II). The method can also be employed in the determination of Cu(II) and Ni(II) in a mixture directly.

Experimental

Apparatus and Reagents : A systronic spectrocolorimeter (type 103) was employed for recording spectra. The pH values of the solutions were measured with a systronic pH meter (type 322).

Standard stock solutions of palladium (II), copper (II), nickel (II) and cobalt (II) were prepared by dissolving appropriate amount of B.D.H. (AnalaR grade) $PdCl_2$, $CuSO_4.5H_2O$, $NiCl_2.6H_2O$ and $CoCl_2.6H_2O$ in double distilled water containing dilute hydrochloric acid (0.5N) and standardized gravimetrically[3]. Ammonium hydroxide-ammonium chloride and acetic acid-sodium acetate were used to prepare buffers of different pH values.

The oxime of 3-bromo-2-hydroxy-5-methylacetophenone[4] was prepared by refluxing its ethanolic solution with hydroxylamine hydrochloride and anhydrous sodium acetate for about two hours and purified by repeated crystallization from ethanol m.p. 198°.

Results and Discussion

It has been observed that the complexes can be extracted into nonaqueous solvents such as chloroform, carbontetrachloride, ethylacetate etc. The colours of the extracted complexes of Pd(II), Cu(II), Ni(II) and Co(II) are yellow, buff, green and yellow respectively. Subsequent studies have been carried out in chloroform, because the extraction was better in chloroform than other nonaqueous solvents.

The method of Vosburg and Cooper[5] was employed to determine the maximum absorption (λ_{max}) and number of the complexes. The absorption measurements show that only one complex is formed which has λ_{max} (nm) 400,640,600 and 400 for Pd(II), Cu(II), Ni(II) and Co(II) complexes respectively.

Effect of pH :

A series of solutions (metal : ligand in 1:4) varying in pH was prepared and the absorbances were recorded after extraction of the complexes into chloroform at their λ_{max}. The range of pH value for no change in absorbance are reported in Table 1. The absorbance of the solutions decrease at higher or lower pH values.

Effect of reagent and ethanol concentration :

It was found that 6 fold excess of the reagent is necessary to attain the full colour development in all the cases under study. The reagent has negligible absorbance at the wave lengths selected for the measurements. The extracted complexes were found to be exhibit constant absorbance for atleast 48 hours.

It was also observed that the extraction of the complexes into chloroform depends upon the concentration of ethanol in aqueous medium. Above 30% (V/V) ethanol, the complex does not completely pass into chloroform layer in one extraction. In view of this 25% (V/V) concentration of ethanol was maintained throughout the work.

TABLE 1—CHARACTERISTICS OF CHELATES OF Pd(II), Cu(II), Ni(II) AND Co(II) WITH BHMAO

Characteristics	Pd(II)	Cu(II)	Ni(II)	Co(II)
Colour	Yellow	Buff	Green	Yellow
λ_{max} (nm)	400	640	600	400
pH range	1.5 – 5.0	4.0 – 8.5	5.0 – 8.0	7.0 – 8.5
Selected pH	2.5	5.5	6.5	7.5
Composition (M : L)	1 : 2	1 : 2	1 : 2	1 : 2
Stability constant	6.8×10^7	4.2×10^7	3.28×10^7	2.525×10^7
Free energy constant (Kcal $mole^{-1}$)	10.77	10.48	10.33	10.18
Beer's law range (ppm)	7.42 – 51.94	8-64	5.87 – 52.83	3.6 – 54.0
Molar extinction coefficient	1000	170	84	640
Sensitivity (ppm)(log Io/I=0.001)	0.106	0.400	0.587	0.180

Composition and stability constant of the complexes :

Job's method of continuous variation[6] was employed. The solutions were mixed in different proportions keeping the total molarity constant. The suitable pH was adjusted (Table 1) of the aqueous phase and the absorbance was measured of extracted complexes in chloroform. The curves between absorbance and metal ion concentration indicate the formation of complexes in which the metal ligand ratio is 1:2. This conclusion is also supported by the mole ratio[7] and slope ratio[8] methods.

The stability constants of the complexes were calculated from the data of the mole ratio method using the usual expressions. The values are reported in Table 1. The changes in free energy (k cal $mole^{-1}$) of the complex formation were also calculated at 27° and reported in Table 1.

Beer's law and physical constants :

The validity of Beer's law (ppm) and sensitivity (metal cm^{-2}) of the reactions for log $I_0/I=0.001$ were calculated and reported in Table 1. The relative mean error was found to be 0.3-0.6%.

General procedure for the determination of metal ions :

A suitable aliquot of metal ion solution containing 20-50 μg of metal ion was introduced on a 100 ml separatory funnel, adjusted to suitable pH value (Table 1) and sufficient excess of the reagent was added to it and mixed thoroughly. The mixture was allowed to stand for 5 minutes. The precipitated complex was extracted 2-3 times with 5 ml portions of chloroform. The extracts were collected in a 25 ml volumetric flask, diluted to the mark with chloroform and the absorbance was measured at λ_{max} against appropriate reagent blank prepared under similar conditions.

Effect of diverse ions :

The influence of diverse ions on the determination of the metal ions using BHMAO was also studied in the usual manner. The difference of ±2% in absorbance value was arbitrarily taken as an interference.

In the case of palladium(II) and copper(II) at 50 ppm ; 2000 ppm CH_3COO^-, NO_3^-, Cl^-, Br^-, SO_4^{2-} ; 1000 ppm Ba^{2+}, Sr^{2+}, Ca^{2+}, Be^{2+}, Cd^{2+}, Mg^{2+}, Fe^{2+}, Na^+,K^+,I^-, 500 ppm Cr^{6+}, citrate, tartrate and 100 ppm Co^{2+}, Ni^{2+}, Mn^{2+} could be tolerated. But Fe^{3+}, VO^{2+},UO_2^{2+} and VO_3^- interfere seriously.

In the case of nickel(II) at 50 ppm ; 2000 ppm Cl^-, Br^-,NO_3^-,SO_4^{2-},CH_3COO^- ; 1000 ppm Na^+,K^+,NH_4^+, I^- ; 500 ppm Ba^{2+},Sr^{2+}, Ca^{2+}, Mg^{2+}, citrate, tartrate, 200 ppm Zn^{2+}, Cd^{2+} could be tolerated. However, Cu^{2+}, Pd^{2+}, Fe^{3+}, UO_2^{2+}, Mn^{2+} and Co^{2+} interfere seriously.

In the case of cobalt(II) at 50 ppm ; 1000 ppm Cl^-, Br^-, NO_3^-, CH_3COO^-, SO_4^{2-} ; 500 ppm Ca^{2+}, Ba^{2+}, Sr^{2+}, Zn^{2+}, Mg^{2+}, Cd^{2+} could be tolerated. But Ni^{2+}, Cu^{2+}, Pd^{2+}, Fe^{3+}, Mn^{2+} interfere seriously.

Simultaneous determination of copper(II) and nickel(II) :

There is a difference of 40 nm in the wavelengths of λ_{max} of the Cu(II) and Ni(II) complexes. In view of this the following equations derived by Sandell[9] for simultaneous determination of the two components were employed for the determination of Cu(II) (A) and Ni(II)(B) :

$$E_1^A C_A + E_1^B C_B = A_1 \text{ (Total absorbance at 640 nm)}$$

$$E_2^A C_A + E_2^B C_B = A_2 \text{ (Total absorbance at 600 nm)}$$

where E_1^4, E_2^4 and E_1^8, E_2^8 the molar extinction coefficients for Cu(II) and Ni(II) complexes at 640 nm and 600 nm respectively are $170(E_1^4)$, $125(E_2^4)$, $84(E_1^8)$ and $70(E_2^8)$ l mole^{-1} cm^{-1}. The results for the determination of Cu(II) and Ni(II) in synthetic mixtures of the two are quite satisfactory.

Acknowledgement

The authors are thankful to Dr. S. P. Gupta, Principal, D. N. College, Meerut, for providing necessary facilities and one of us (SRM) thanks the C.S.I.R., New Delhi, for the award of Junior Research Fellowship.

References

1. K. Lal, J. Singh and S. P. Gupta, *J. Inorg. Nuclear Chem.*, 1978, 40, 359; *Acta Chim. Acad. Sci. Hung.*, 1977, 95, 233.
2. K. Lal and S. P. Gupta, *Indian J. Chem.*, 1976, 14A, 260; *Rev. Chem.*, (Roumania), 1976, 27, 657.
3. A. I. Vogel, "*A Text Book of Quantitative Inorganic Analysis*", Longman, London, 1968.
4. M. G. Marathey and K. G. Gore, *J. Univ. Poona Sci. & Tech.*, 1954, 6, 77.
5. W. C. Vosburg and G. R. Cooper, *J. Amer. Chem. Soc.*, 1941, 63, 437.
6. P. Job, *Ann. Chem.*, 1928, 9, 113.
7. J. H. Yoe and A. L. Jones, *Ind. Eng. Chem. Anal. Ed.*, 1944, 16, 111.
8. A.E. Harvey and D.L. Manning, *J. Amer. Chem. Soc.*, 1950, 72, 4448.
9. E. B. Sandell, "Colorimetric Determination of Traces of Metals", Interscience, New York, 1959, p. 102.

Bromatometric Estimation of Ascorbic Acid Using Azine and Oxazine Dyes as Indicators*

P. V. RAMANA, K. MOHANA RAO

and

N. VENKATESWARA RAO

Andhra University, Waltair-530 003

Manuscript received 14 June 1979, accepted 30 November 1979

THE indicators that have been reported for the bromatometric estimation of ascorbic acid are: *p*-ethoxychrysoidine[1]; starch-iodide[2], aminophenoxazones[3], naphthol blue black and variamine blue[4], and chlorpromazine, promazine, perazine and diethazine[5]. Of these, only *p*-ethoxychrysoidine has been utilised for the titrimetric determination of ascorbic acid in the pure form as well as medicinal preparations[1]. The present communication describes the use of eleven azine and oxazine dyes, Neutral Violet(NV), Neutral Red(NR) Azocarmine G (ACG), Azocarmine B (ACB), Wool Fast Blue GL (WFBGL), Nigrosin (NG), Capri Blue (CB), Solochrome Prune AS (SPAS), Gallamine Blue (GB), Celestine Blue (CLB), and Meldola's Blue (MB) (Colour Index Nos. 50030, 50040, 50085, 50090, 50320, 50420, 51015, 51040, 51045, 51050 and 51175 respectively), as indicators in the titrimetric estimation of ascorbic acid with potassium bromate in hydrochloric and sulphuric acid media and the application of the methods for the determination of ascorbic acid content of commercial vitamin C tablets. In this connection, it may be mentioned that the azine dyes have been used for the titration of arsenic (III) with potassium bromate[6].

The advantages of the indicators now reported are: (1) they can be added at the beginning of the titration, (2) the titration can be performed even in the absence of added potassium bromide, and (3) three of the indicators, ACG, ACB and WFBGL, function reversibly and can therefore be employed for the reverse titrations, i.e., titrations of potassium bromate with ascorbic acid, also; the indicators reported earlier have to be added towards the close of the titration, presence of added potassium bromide is necessary, and except variamine blue, other indicators are not suitable for the reverse titrations.

Experimental

Approximately 0.1*N* solutions of potassium bromate and ascorbic acid were prepared and standardised. A small quantity (0.5 g per litre) of E.D.T.A. was added as stabiliser for the ascorbic acid solutions. Solutions (0.1%) of the azine and oxazine dyes were prepared in deionised water from the following samples: NV: George T. Gurr, NR: E. Merck, ACG and NG: Fluka, WFBGL: Bayer, CB: Chroma, ACB, SPAS, GB, CLB and MB: E. Gurr.

Procedure:

Ascorbic acid solution (3 – 10 ml of 0.1 *N*) is treated with enough 1:1 hydrochloric or sulphuric acid, so as to give an acidity of 1.0*M* hydrochloric acid or 2.5*M* (3.0 with SPAS, CB and GB) sulphuric acid when diluted to 50 ml, and the following amount of the indicator solution:

NR, ACG, WFBGL, CB, SPAS, GB and MB: 0.1 ml, ACB and NG: 0.25 ml, NV and CLB: 0.5 ml.

The mixture is then titrated with 0.1 *N* potassium bromate solution and the end point is indicated by the decolourisation of the titration mixture.

The colour changes at the end points are very sharp and the results obtained are in excellent agreement with those obtained by other methods.

The following indicators function satisfactorily in titrations involving dilute (0.01*N*) solutions of ascorbic acid and potassium bromate also.

* Presented at the Annual Convention of Chemists, Waltair, December 27-31, 1978.

HCl medium : (1.0*M*) : NV, NR, ACG, ACB, WFBGL, CB, SPAS, CLB, GB and MB.

H_2SO_4 medium : (1.0*M*) + 5 ml of 10% KBr solution : NV, NR, WFBGL, CLB, SPAS and GB

NG does not function satisfactorily in any acid medium.

Titrations of 0.1*N* solutions do not require any indicator correction whereas those involving 0.01*N* solutions require the following indicator corrections :

HCl medium : NV, NR, ACG, ACB and WFBGL : 0.02 ml ; CB : 0.04 ml ; GB : 0.06 ml ; SPAS, CLB and MB : 0.10 ml

H_2SO_4 medium : NV, NR, WFBGL and CLB : 0.04 ml ; SPAS and GB : 0.10 ml.

Reverse titrations : Variamine blue[7] is the only indicator proposed for the reverse titrations, i. e., titrations of potassium bromate with ascorbic acid. Our investigations have shown that ACG, ACB and WFBGL can be satisfactorily employed in the titrations of potassium bromate with ascorbic acid in 1.5 – 1.75*M* sulphuric acid medium. In these titrations, the indicator has to be added towards the close of the titration, and waiting for about 30-40 sec is necessary in the vicinity of the end point. The end point is taken as that at which the colour of the dye, pink with ACG and ACB and blue with WFBGL, is imparted to the titration mixture and is stable for more than 30 sec.

Attempts to perform the reverse titrations in hydrochloric acid medium yielded erratic results.

Mechanism of indicator action ; The functioning of the indicators in these titrations can be explained to be due to the bromination of the dye indicators, in view of the liberation of bromine and discharge of the colours of the dyes at the end points. Separate experiments have indicated that these dyes get decolourised by bromination. Further support to this mechanism is provided by the work of Bognar[8] involving the use of the azine dyes, Azocarmine B, Azocarmine BX, Azocarmine G, Azocarmine GX, Rosindulin G, Rosindulin GG, and Rosindulin 2G, as indicators in the titration of arsenic (III) and antimony (III) with a solution of bromine.

In view of the advantages associated with the use of the azine and oxazine dye indicators in the bromatometric titrations of ascorbic acid, we have applied the methods now developed for the determination of ascorbic acid content of commercial vitamin C tablets. Solutions of the tablets were prepared as described in an earlier method[9] and aliquots of the solutions were titrated with 0.1*N* potassium bromate solution using any one of the azine and oxazine dye indicators. A similar aliquot was titrated using *p*-ethoxychrysoidine as indicator as per the method of Schulek *et al*[1]. Typical results obtained are given in Table 1.

TABLE 1 – DETERMINATION OF ASCORBIC ACID IN VITAMIN C TABLETS

Indicator and amount of ascorbic acid found, in g, in 6 tablets[φ]		
Schulek's method[1]	ACG[a]	SPAS[a]
2.95±0.01	2.95±0.01	2.95±0.01
2.97±0.01	2.98±0.01	2.98±0.01
3.10±0.01	3.09±0.01	3.10±0.01
2.94±0.01	2.94±0.01	2.93±0.01

φ These were market products of different manufacturers.
a Similar results were obtained with the remaining nine indicators also.

Acknowledgement

We are grateful to the U.G.C. for financial assistance to N.V.R. and to the Andhra University, Waltair, for the award of a Research Fellowship to K.M.R.

References

1. E. SCHULEK, J. KOVACS and P. ROZSA, *Z. Analyt. Chem.*, 1941, **121**, 17.
2. L. SZEKERES, E. SUGAR and E. PAP, *Z. Analyt. Chem.*, 1958, **163**, 32.
3. E. RUZICKA, *Coll. Czech Chem. Commun.*, 1964, **29**, 2244.
4. G. SITARAMA SASTRY, Ph. D. thesis, 1965, Andhra University, Waltair, p. 283.
5. PUZANOWSKA-TARASIEWICZ and HELENA, *Chemia Analit.*, 1973, **18**, 953.
6. N. V. RAO and P. V. RAMANA, *Z. Analyt. Chem.*, 1977, **285**, 125.
7. G. SITARAMA SASTRY, Ph.D. thesis, 1965, Andhra University, Waltair, p. 206.
8. J. BOGNAR, *Nehezip. Musz. Egy.*, *Miskol. Kozl.*, 1974, **20**, 11.
9. N. V. RAO, K. MOHANA RAO, K. R. K. MURTY and G. SURYANARAYANA, *Indian J. Pharm. Sci.*, 1978, **40**, 128.

Spectrophotometric Microgram Determination of Lead

P. K. JAISWAL * and R. K. RAO

Food Research and Standardisation Laboratory, Navyug Market, Ghaziabad-201 001, INDIA

Manuscript received 24 July 1979, accepted 29 December 1979

EXTENSIVE work on the determination of lead present as contamination has been carried out by various workers[1–4]. Lead as usual with other metals becomes toxic in nature beyond certain conce-

* To whom correspondence may be addressed at the Directorate of Marketing and Inspection, New Secretariat Building, Nagpur-440 001.

stration level in a variety of food stuffs. The conventional methods followed for determination of lead in food stuffs, comprise visual comparative colour developments with ammonium acetate, potassium cyanide and sodium sulphide or hydrogen sulphide in ammoniacal medium. However, these methods lack precision due to personal error. In this communication, an improved and precise method for determining lead in trace amounts by absorbance measurement, after eliminating the interfering inorganic and organic materials by standard methods is described.

Materials and Method :

Materials : All chemicals used were of AR grade. Carl Zeiss VSU2-P spectrophotometer was used for measuring the absorbance. Doubly distilled water over alkaline potassium permanganate in all glass apparatus was used throughout the experiments.

Procedure : Lead as lead nitrate was allowed to form a brown complex with potassium cyanide (1 ml, 10%) and sodium sulphide (0.5 ml, 10%) in ammoniacal medium (3 ml. ammonia, sp. gr. 0.91). The absorbance of which was recorded after diluting the contents to 50 ml. with water at 290 nm. Lead from 1-12μg per ml was found to obey Beer's Law. The amount of lead determined was computed from a standard calibration curve. Blank experiments were also carried out simultaneously under similar identical conditions. The results are given in Table 1.

TABLE 1—DETERMINATION OF LEAD

Lead (μg) Taken Per ml.	Lead (μg) Found Per ml.	Absorbance*	% Error
1.00	0.98	0.068	−2.00
1.50	1.52	0.10	+1.33
2.00	1.97	0.130	−1.50
3.00	3.03	0.20	+1.00
4.00	4.02	0.264	+ .50
6.00	6.02	0.382	+0.33
8.00	7.92	0.53	−1.00
9.00	8.91	0.585	−1.00
10.00	10.15	0.65	+1.50
12.00	12.15	0.90	+1.25

* Mean of five determinations.

All the studies were made at wavelength 290 nm and slit width 0.3 mm.

Total volume of the complex solution was always raised to 50 ml. in all the experiments.

Results and Discussion

From the observations, it is evident that the method developed may be suitable for determining lead contents in food stuffs in p.p.m. level after eliminating interfering materials. Various experiments performed show that excess of potassium cyanide (10ml, 10%), ammonia (10 ml, sp. gr. 0.91) and sodium sulphide (1 ml. 10%) have practically no effect on the absorbance of the lead complex.

It has, however, been noted that the complex decomposes on standing, and thus it is suggested that absorbance should be measured immediately after the complex formation or within 10-20 minutes.

An attempt was made to replace sodium sulphide by water saturated with hydrogen sulphide, which met with no success.

References

1. I.U.P.A.C. Commission for the determination of trace elements in food, *Pure & Appl. Chem.*, 1965, 10, 71.
2. E. F. DALTON and A. J. MALANOSKI, *J. Ass. of Analyt. Chemistry*, 1969, 52, 1035.
3. R. GAEWSKA, M. NABRZYSKI and E. LIPKA, *Bromatol Chem. Toksykol*, 1976, 9, 1.
4. T. ZAWADZKA, *Rocznpanst. Zakl. Hig.*, 1976, 27, 411.

Polarographic Behaviour of *Cis-Trans* Isomers of Platinum(II) Complex of the Type $[Pt(NH_3)(NO_2)Cl_2]^-$

K. S. PITRE

Chemistry Department, University of Saugar, Sagar-470 003, M.P.

Manuscript received 4 May 1979, accepted 29 December 1979

THE ligand arrangement around an atom after a substitution reaction may or may not be similar to that of the starting material even for inert complexes. The chemistry of Platium(II) is exceptional in this respect, in that the product of a substitution reaction can be predicted with confidence. The *Cis* and *Trans* isomers of Platinum (II) complex having formula $[Pt(NH_3)(NO_2)Cl_2]$ have been prepared and examined polarographically. It is observed that each of the isomers gives a separate reversible cathodic polarographic wave. The value of $E_{0.5}$ for *cis*-isomer = − 0.105V, Vs SCE and that for *trans*-isomer = − 00.140V Vs SCE. In both the cases 1*M* kcl is used as supporting electrolyte.

Platinum(II) is a very well known ion for the formation of *cis-trans* isomers. In the case of Platinum(II) the product of a substitution reaction can be predicted with confidence.

The polarographic technique can be successfully employed for the identification of *cis-trans* isomers of metal complexes. Crow and Westwood[1,2] have prepared the *cis-trans* isomers of Rhodium (III) and Cobaltic ions separately and got two distinct waves for the two forms of the complex.

The author has prepared the *cis-trans* isomers of Platinum (II) complex of the type $[Pt(NH_3)(NO_2)Cl_2]^-$ and examined them polarographically. The results of his observation are given in this paper.

Experimental

All the reagents used were of AnalaR/BDH grade. The solutions were prepared in conductivity water. An automatic pen recording C.I.C. (India) polarograph was used to record the polarograms. The *p*H of the solutions was measured using a Phillips *p*H-meter.

All the observations were made at room temperature, 27°.

The *cis* and *Trans* isomers of Platinum(II) complex of the type $[Pt(NH_3)(NO_2)Cl_2]^-$ were prepared[3] and their polarograms were recorded[4]. The ionic strength and the *p*H of the solutions was kept constant ; using KCl solution and a buffer solution for their respective adjustments.

Results and Discussion

It is observed that each of the *cis* and *trans* isomers of $[Pt(NH_3)(NO_2)Cl_2]^-$ gives a separate reversible cathodic polarographic wave. The details of the polarographic study are given below :

Supporting-Electrolyte	– 1 *M* KCl
Maximum suppressor	– 0.001% gelatin
Platinum (II)	$-5\times10^{-4}M$
Ammonia	$-5\times10^{-4}M$
NO_2^-	$-5\times10^{-4}M$

Drop time = 3.1 sec. Sensitivity = 0.3×3, μA/mm μ = 1.0, Temperature = 27° and *p*H = 6.68 ± 0.2.

TABLE 1

1. $[Pt(NH_3)(NO_2)Cl_2]^-$ *cis*	$E_{0.5} = -0.105$ V Vs SCE
2. $[Pt(NH_3)(NO_2)Cl]^-$ *trans*	$E_{0.5} = -0.140$ V Vs SCE

The plot of $\log\frac{I}{Id-I}$ Vs E for each of the two forms is a straight line whose slope is 54 ± 1.5 mv for the *cis* form and 56 ± 1.1 mv for the *trans* form indicating a reversible one electron reduction for both the cases. It is observed that for each of the two forms of the complex the polarographic diffusion current is proportional to its concentration and the Id/C value is 4.9 ± 0.2 for the *cis* complex and 5.6 ± 0.1 for the *trans* complex.

It is quite clear from the above data that the polarographic behaviour of the two isomers is sufficiently distinct for identification purpose. The *cis* isomer is reduced at a more positive potential than the *trans* form, which is an excellent agreement with results of Crow and Westwood who have reported a similar behaviour of *cis-trans* $[CO(en)_2(NO_2)]^+$ complexes. A qualitative explanation for the observed shift in the half-wave potential for the two forms is based on a simple electrostatic argument that the preferred orientation of the *cis*-complex is due to the large internal dipole at a positive surface.

Acknowledgement

The author is thankful to Prof. S. S. Nigam, Head, Chemistry Department, University of Saugar for providing laboratory facilities.

References

1. D. R. CROW, *Inorg. Nuclear Chem. Lett.*, 1969, 5, 291.
2. D. R. CROW and J. V. WESTWOOD, 'Polarography of metal complexes', Academic Press, London 1969, p. 154.
3. S. F. A. KETTLE, 'Co-ordination compounds', The English Language Book Society and Nelson, 1975, p. 40.
4. A V. MAHAJANI and K. S. PITRE, *J. Indian Chem. Soc.*, 1976, 53, 97.

Non-equilibrium Thermodynamic Studies of Electrokinetic Effects. Part XIII. Relaxation Time, Entropy Production Studies in Ethylene Glycol Water Mixtures

R. L. BLOKHRA and S. K. AGGARWAL

Department of Chemistry, Himachal Pradesh University, Simla

and

V. P. SHARMA

Department of Chemistry, Panjab University, Chandigarh

Manuscript received 8 January 1979, revised 29 August 1979, accepted 31 December 1979

THE entropy production in irreversible processes such as transport processes (electro-osmosis in the present case) has attracted the attention of a number of workers[1-8]. The character of entropy production, both in steady and non-steady state is now better understood in terms of non-equilibrium thermodynamics[4,5]. According to Prigogine[5], the entropy production is minimum in the steady state. However, the theory of minimum entropy production is valid only when linear laws and Onsager's reciprocal relations hold good. Glansdorff[5] and Prigogine[4] have given a new theorem which states that for both linear and non-linear

egions the function

$$m = -\sum_i J_i \dot{X}_i > 0$$

he equality holding for the steady steate. $\dot{X}_i$ is the time lerivatives of the force X_i, J_i being the corresponding low. One of the purposes of the present communiation is to examine the validity of the generalization n case of electro-kinetic phenomena. Another object s to determine the relaxation time Γ, for the electrosmosis as defined by Haase[6]. It has been estimated or different water-ethyleneglycol mixtures from the ormula giving the dependence of electro-osmotic ressure on time during the approach to steady state.

Experimental

Ethylene glycol was purified by vacuum distillation ifter drying it over calcium oxide, calcium sulphate and odium metal and stored in sealed bottles.

Apparatus and Procedure :

The apparatus and the experimental set up adopted or the investigation were similar to those described earlier[7]. The experiments were carried out in an air hermostat having fluctuations of the order of 0.05°. The electric potential across the disc was applied hrough grey platinum electrodes in order to avoid he decomposition or oxidation of the system being tudied.

Results and Discussion

The relaxation time, Γ, for electro-osmosis is lefined as[6]

$$\Gamma = q_0 \delta / (2 q \rho g \beta) \quad \ldots \quad (1)$$

where ρ is the density of the liquid, g the gravitational acceleration, q the cross-section area of the diaphragm, δ the thickness of the diaphragm, β the permeability and q_0 is the cross-section of the capillary tube in which the liquid rises during the electro-osmotic flow. Using the expression it has been deduced that the change in the height of the liquid column with time in the vertical tube is given by

$$\frac{dh}{dt} = (h_\infty - h)/\Gamma \quad \ldots \quad (2)$$

Where h_∞ is the height level corresponding to the steady state of the electro-osmotic pressure and h is the height at time t.

Integrating the equation (2) and taking into account the initial condition that $h = h_0$ for $t = o$, we obtain

$$\ln(h_\infty - h_0) - \ln(h_\infty - h) = t/\Gamma \quad \ldots \quad (3)$$

Thus Γ can be estimated from the slope of the linear plot of $\ln(h_\infty - h)$ versus t. We found linear plots in all the mixtures and a sample plot is shown in Fig 1. The values obtained are given in Table 1.

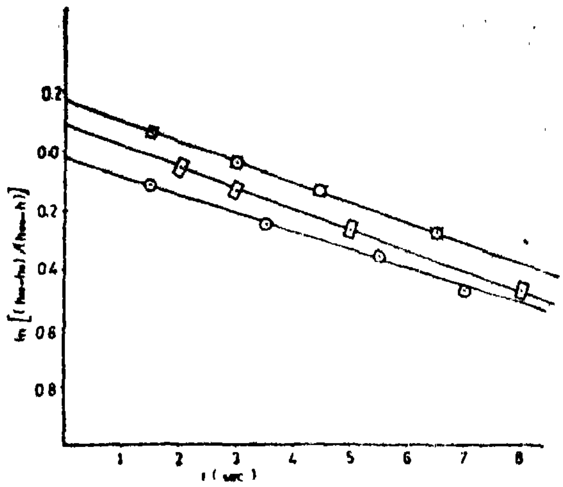


Fig. 1. Plot for the evaluation of the relaxation time.
⊙–⊙–⊙ 50% EG–H_2O
⊙– –⊙– –⊙ 60% EG–H_2O
⊡–⊡–⊡ 70% EG–H_2O

TABLE 1—RELAXATION TIME FOR ELECTRO-OSMOTIC FLOW AT 100 VOLTS WITH ETHYLENEGLYCOL-WATER MIXTURES AT 25°C

Percentage (w/w) of ethyleneglycol	30	50	60	70
Relaxation time (Γ)	0.06	0.08	0.07	0.03

Entropy production in electro-osmosis :

Recently Haase[8] dealt with the time dependence of the dissipation function/entropy function in electro-osmotic experiments for systems approaching a stationary (steady) state. In a steady state, the pressure difference, $\triangle P$, and the electric potential difference, $\triangle\phi$, do not depend on time. It has also been observed that J and d $(\triangle P)$1dt have opposite sign[6,9] except in the stationary state, where both the quantities vanish. Thus, we have

$$J \triangle P < 0 \quad \text{or} \quad -J \triangle P > 0 \quad \ldots \quad (4)$$

The equality sign applies to the steady state. Further according to the generalisation of Glansdorff and Prigogine for electrokinetic effects it can be written as

$$m = -(I \triangle \dot{\phi} + J \triangle \dot{P}) \quad \ldots \quad (5)$$

In the above equation the quantity $J \triangle \dot{P}$ is that part of the rate of increase of the dissipation function (product of thermodynamic temperature and entropy production) which is due to the change of the force for fixed values of the fluxes. The evolution criterion states that this quantity is negative or zero (for a steady state) for any distance from equilibrium provided the temperature is kept constant (a condition fulfilled here), the electric potential difference is fixed $(\triangle\dot{\phi} = o$, see above) and the total system is closed (a condition fulfilled approximately). In the case of electro-osmotic pressure difference the relation (5) reduces to (4) because

$\Delta\phi$ is kept constant in these experiments. $\dot{J}$ and $\Delta\dot{P}$ were calculated from the slope of the curve obtained by plotting the rise of liquid against time. The values of $J\Delta\dot{P}$ for 30% ethylene glycol are plotted versus time in Fig. 2.

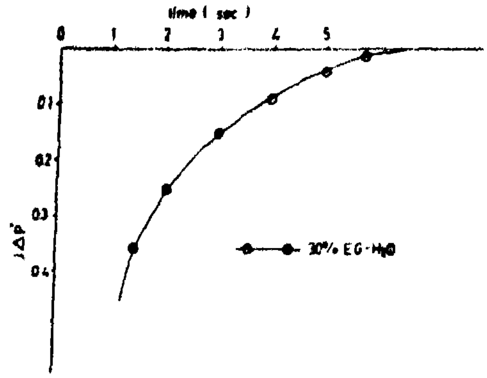


Fig. 2. Plot of J∆P versus t for EG—Water mixture.

The curve approaches the time axis asymptotically proving the theorem in the case of electro-osmotic flow and also it gives the evolution of entropy production. Similar plots have been obtained for other mixtures.

Acknowledgement

One of the authors (S. K. \.) is highly grateful to C. S. I. R., New Delhi (India) for the award of a Post-doctoral Fellowship.

References

1. J. G. Kirkwood and B. Crawford, *J. Phys. Chem.*, 1952, **56**, 1048.
2. W. W. Wood and J. G. Kirkwood, *J. appl. Phys.*, 1957, **28**, 395.
3. R. P. Rastogi and R. C. Srivastava, *J. Chem. Phys.*, 1960, **33**, 79.
4. P. Glansdorff and I. Prigogine, *Physca's, Crav.*, 1954, **20**, 773.
5. I. Prigogine. In thermodynamics of irreversible processes by S.R. De Groot (North Holland Publishing Co., Amsterdam), 1952.
6. R. Haase, *Z. Phys. Chem. N.F.*, 1976, **103**, 235.
7. R. L. Blokhra, M. L. Parmar and V. P. Sharma in M. Kerker (Ed), Colloid and Interface Sci., Vol. IV, Academic Press, New York, 1976, 259.
8. R. Haase, *Z. Phys. Chem. N.F.*, 1976, **103**, 247.
9. R. C. Srivastava and R. L. Blokhra, *Indian J. Che*3.. 1963, **1**, 156.

AUTHOR INDEX

J. Indian Chem. Soc.,
Vol. LVII, March 1980, pp. 241-243

Complex Formation of Co(II) with N-Benzenesulphonyl-L-Cysteine*

G. N. MUKHERJEE** and P. DHAR

Department of Pure Chemistry, Inorganic Chemistry Laboratory, University College of Science, 92, Acharya Prafulla Chandra Road, Calcutta-700 009, India

Manuscript received 8 November 1979, accepted 30 December 1979

*p*H-metric study of the reaction between Co(II) and N-benzene-sulphonyl-L-cysteine $C_6H_5SO_2NHCH(COOH)CH_2SH$ indicated the formation of 1 : 1 and 1 : 2 metal : ligand complexes having the co-ordination patterns [CoNS] and [CoN_2S_2] respectively. Complete deprotonation of the -COOH group before the start of complex formation suggested non-involvement of this group in co-ordination. Stepwise formation constants (K_1 and K_2) and the successive acid dissociation constants (k_{2NH}, k_{1NH}) of the 1 : 2 complex have been evaluated by following the procedure of Irving and Rossotti. Values of $\log K_1$, $\log K_2$, pk_{2NH} and pk_{1NH} are 6.03±0.03, 5.60±0.03, 11.55±0.04 and 13.30±0.04 respectively at 30±0.5°, in 50% (v/v) water-dioxan medium having ionic strength 0.50*M* ($NaClO_4$). The pk_{COOH}, pk_{SH} and pk_{NH} values of the ligand have been found to be 4.43±0.02, 11.05±0.02 and 13.44±0.04 respectively under identical condition.

Enhancement of acidity the imido (-NH-) group in the 1 : 2 complex indicated the formation of Co-N bonds. The extent of enhancement was, however, small compared to the corresponding Zn(II) compound (found pk_{2NH} 8.20 and pk_{1NH} 10.30), as probably Co(II) formed its best bonds with (Thiol) sulphur.

STUDY of the interaction of metal ions of different classes with the ligand N-benzenesulphonyl-L-cysteine $C_6H_5SO_2NHCH(COOH)CH_2SH$, here after NBSC or ($\genfrac{}{}{0pt}{}{HS}{HN}$> RCOOH) or LH_3, having suitably placed hard (-COOH), borderline (-NH-) and soft (-SH) co-ordinating groups may provide valuable information about the specificities of the metal binding sites in proteines which have these types of groupings in their primary structures. The ligand NBSC used all its three donor sites, (-COOH,-NH-,-SH) in complexing borderline metal ions. viz., Zn(II) and Cd(II)[1a,b] but it used only-NH-and-SH ends in complexing a soft metal ion, Hg(II)[1c]. With a softer metal ion, Ag(I), the ligand formed a 1 : 1 metal : ligand complex at very low *p*H values (2.5-3.0) using only the soft mercapto (-SH) group[2]. In the present work the interaction of Co(II) ion with the ligand NBSC has been followed *p*H-metrically at 30±0.5° in 50% (v/v) water-dioxan medium maintaining a constant ionic strength, μ=0.50*M* ($NaClO_4$).

Experimental

The ligand NBSC was prepared and purified by the procedure described earlier[1a]. All other reagents were either of A. R. quality or properly purified and their solutions were made in double distilled CO_2-free water and purified dioxan[3].

*p*H-metric titrations of the following solutions

(i) 0.01(*M*) $HClO_4$,
(ii) 0.01(*M*) $HClO_4$+0.01(*M*) NBSC,
(iii) 0.01(*M*) $HClO_4$+0.002(*M*) Co(II),
(iv) 0.01(*M*) $HClO_4$+0.003(*M*) Co(II),
(v) 0.01(*M*) $HClO_4$+0.01(*M*) NBSC+0.002(*M*) Co(II),
(vi) 0.01(*M*) $HClO_4$+0.01(*M*) NBSC+0.003(*M*) Co(II),

were performed in 50% (v/v) water-dioxan medium with a standard NaOH solution in the same solvent medium while maintaining the ionic strength constant at 0.50(*M*) using requisite amount of $NaClO_4$.

*p*H-measurements were made with a Cambridge *p*H-meter (Portable Type) having a glass electrode of 1-13 *p*H range and a saturated Calomel electrode connected to the cell by means of an agar-2(*M*) $NaNO_3$ bridge. The meter was calibrated using standard 0.01(*M*) $HClO_4$ solution, phthalate buffer and borate buffer solutions with appropriate temperature corrections.

*Abstract presented at the Annual Convention of Chemists, Kurukshetra, 1979, Indian Chemical Society.
**To whom correspondence may be addressed.

Titration curves, pH (volume of alkali), were drawn (Fig.1) and the necessary concentration variables were calculated following the procedure of Irving and Rossotti[4a].

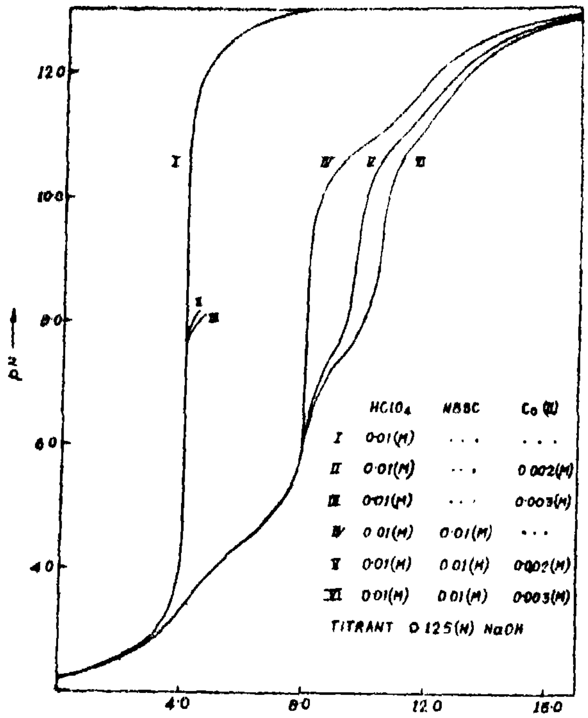


Fig. 1.

Results and Discussions

I. Stepwise Acid Dissociation of NBSC :

Consumption of more than two equivalents of alkali per mole of the ligand NBSC in the pH range 2.2 to 12.8 in the titration of solution (iv) indicated three successive steps of its acid dissociation which can be represented by the following equilibria :

$$\begin{matrix}HS\\ HN\end{matrix}\!\!>RCOOH \overset{k_{COOH}}{\rightleftharpoons} \begin{matrix}HS\\ HN\end{matrix}\!\!>RCOO^- + H^+ \quad \dots (1)$$

$$\begin{matrix}HS\\ HN\end{matrix}\!\!>RCOO^- \overset{k_{SH}}{\rightleftharpoons} \begin{matrix}\bar{S}\\ HN\end{matrix}\!\!>RCOO^- + H^+ \quad \dots (2)$$

$$\begin{matrix}\bar{S}\\ HN\end{matrix}\!\!>RCOO^- \overset{k_{NH}}{\rightleftharpoons} \begin{matrix}\bar{S}\\ \bar{N}\end{matrix}\!\!>RCOO^- + H^+ \quad \dots (3)$$

k_{COOH}, k_{SH} and k_{NH} are the successive acid dissociation constants. The plot of $\bar{n}_H$ (the average number of protons bound to the ligand ion, $\begin{matrix}S\\ N\end{matrix}\!\!>RCOO^{=}$) against pH showed that the steps (1), (2) and (3) were independent of one another and, therefore, the constants k_{COOH}, k_{SH} and k_{NH} were evaluated by curve fitting method[5a] for one step system and also by the method of linear plots. The refined pk_{COOH}, pk_{SH} and pk_{NH} values ars stated in Table I.

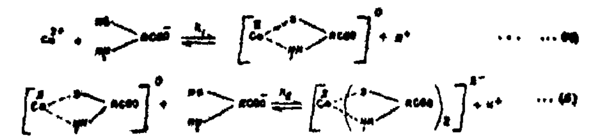
II. Formation of Co(II) Complexes of NBSC :

The nature of the pH titration curves of solutions (ii), (v) and (vi) Fig. 1 indicated the liberation of one equivalent of acid per mole of the ligand below pH = 6.5 both in the absence and in the presence of Co(II) ion. Thus the first step acid dissociation (1) of the ligand (i.e. deprotonation of the-COOH group) was not influenced by Co(II) ion. Therefore, the-COOH group was not involved in the interaction of NBSC with Co(II) ion. Analysis of the titration data in the pH range from 6.0 to 9.5 according to the procedure of Irving and Rossottt[4a] showed that, for the association of each mole of the ligand species to Co(II) ion one equivalent of acid per gm ion of Co(II) was liberated. Free metal ion curves (II) and (III), Fig. 1, showed that the formation of hydroxo complexes were negligible at the early stages of complex formation. Therefore, from a consideration of the pk_{SH} and pk_{NH} values of the ligand (Table 1) and the pH range of the buffer region in the titration of solutions (v) and (vi), stepwise complex formation of Co(II) with the ligand

TABLE 1—PROTON-LIGAND AND Co(II)-LIGAND STABILITY CONSTANTS OF NBSC COMPLEXES AT 30±0.5°C, IN 50% (v/v) WATER-DIOXAN MEDIUM HAVING IONIC STRENGTH 0.5M ($NaClO_4$)

	Co(II)	Zn(II)[1a,b]	Hg(II)[1c]	NBSC	
$\log K_1$	6.03 ±0.03	8.33	–	pk_{COOH}	= 4.43±0.02
$\log K_2$	5.60 ±0.03	7.22	—	pk_{SH}	=11.05±0.02
pk_{2NH}	11.55 ±0.04	8.20	10.49	pk_{NH}	=13.44±0.04
pk_{1NH}	13.30 ±0.04	10.30	11.55		

ions, $\genfrac{}{}{0pt}{}{HS}{HN}>RCOO^-$, was assumed to take place through deprotonation of the thiol (-SH) group according to the equations (4) and (5).



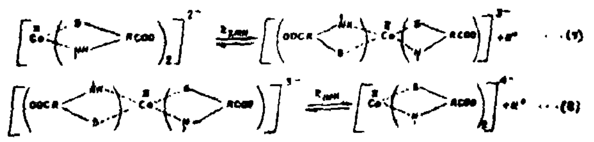
where K_1 and K_2 are the two step-formation constants. The complex formation curve, $\bar{n}_{LH}$ (pLH) (where LH stands for $\genfrac{}{}{0pt}{}{S}{NH}>RCOO^-$ ion) indicated that the steps (4) and (5) were overlapping. The $\log K_1$ and $\log K_2$ values were, therefore, refined by projection strip method[5b] and also by the method of linear plots employing suitable forms of the function :

$$\bar{n}_{LH}=(K_1[LH]+2K_1K_2[LH]^2)/(1+K_1[LH]+K_1K_2[LH]^2) \quad \ldots (6)$$

Refined values of $\log K_1$ and $\log K_2$ are stated in Table 1.

III. Acid dissociation of the Complex bis-N-benzenesulphonyl-L-cysteinato Co(II) ion. :

pH metric titration curves of solution (v) and (vi) Fig. 1, indicated further liberation of more than one equivalent of acid per gm ion of Co(II) at pH values greater than 10.0, i.e., after $\bar{n}_{LH} = 2$ and this was accounted for by assuming stepwise acid dissociation of the complex ion, according to (7) and (8).



where k_{2NH} and k_{1NH} are the successive acid dissociation constants. Average number $\bar{n}_h$) of protons qound to the complex ion $[Co(\genfrac{}{}{0pt}{}{S}{N}>RCOO)_2]^{4-}$, were calculated[4a] assuming all the Co(II) ions in the form of the 1 : 2 metal : ligand complex in the pH range from 10.0 to 12.8. From the $\bar{n}_h$ $(p$H) plot it was found that the acid dissociation steps (7) and (8) were overlapping. The refined values of k_{2NH} and k_{1NH} were evaluated by the method of linear plot employing suitable forms of the function :

$$\bar{n}_h=\frac{(2[H^+]^2/k_{2NH}k_{1NH}+[H^+]/k_{1NH})}{([H^+]^2/k_{2NH}k_{1NH} + [H^+]/k_{1NH} + 1)} \quad \ldots (9)$$

Refined pk_{2NH} and pk_{1NH} values are stated in Table I.

Limits of error[5a] in the determination of the constants were found out by comparing the experimental curves : $\bar{n}_H$ $(p$H), $\bar{n}_{LH}$ $(p$LH) and $\bar{n}_h$ $(p$H) with the calculated ones obtained from apppropriate function using refined values of the constants and experimental values of pH or pLH as the case may be. Standard deviations[4b] were calculated and were found to be $\pm 0.015 \sim \pm 0.020$.

Formation constants of Co(II) complexes are found to be lower than those of the corresponding complexes of Zn(II)[1a,b] under identical condition. This may be due to more favourable entropy effect arising from tridentate chelation in the case of Zn(II). Enhancement of acidity of the imido (-NH-) group from $pk_{NH}=13.44$ (ligand) to $pk_{2NH}=11.55$ and $pk_{1NH}=13.30$ in the 1 : 2 Co(II) : ligand complex indicates the formation of metal-nitrogen bonds[6]. But as in the case of *bis*-N-benzenesulphonyl-L-cysteinato Hg(II)[1c], the enhancement of imido acidity in the present case was also small compared to that in the corresponding Zn(II) compound[1a,b]. This may probably be due to the fact that Co(II) being a softer Lewis acid than Zn(II)[7], forms much stronger bonds with thiol sulphur than those with imido nitrogen because of the ability[8] of thiol sulphur to form much stronger σ-bonds due to its higher polarisability, together with π-bonds by back receiving of electron density from metal ion $d\pi$ orbitals in to the vacant $d\pi$ orbitals of its own.

Acknowledgement

Authors' grateful thanks are due to Professor N. N. Ghosh, Retired Professor of Pure Chemistry, Caclutta University for his kind encouragement.

References

1. N. N. Ghosh and G. N. Mukherjee, (a) *Indian J. Chem.*, 1974, **12**, 636 ; 1975 **13**, 1206, (b) *J. Indian Chem. Soc.*, 1975, **52**, 1037, (c) *J. Indian Chem. Soc.*, 1978, **55**, 313.
2. P. Dhar and G. N. Mukherjee, *J. Indian Chem. Soc.*, 1979, **56**, 1258.
3. A. I. Vogel, "*Text Book of Practical Organic Chemistry*" (*E.L.B.S.*), 1968, p. 177.
4. H. M. Irving and H. S. Rossotti, *J. Chem. Soc.*, (a) 1954, 2904 ; (b) *J. Chem. Soc.* 1953, 3397.
5. F. J. C. Rossotti and H. S. Rossotti, "*The Determination of Stability Constants*", McGraw-Hill, London, 1961, (a) p. 87 ; (b) p. 99 ; (c) p. 88.
6. N. N. Ghosh and G. N. Mukherjee, *Z. Physik. Chem.* (*N.F.*), 1974, **88**, 69.
7. M. Misono, E. Ochiai, Y. Saito and Y. Yeneda, *J. Inorg. Nuclear Chem.*, 1967, **29**, 2685.
8. S. E. Livingstone, *Quart. Rev.*, 1965, **19**, 386.

J. Indian Chem. Soc.,
Vol. LVII, March 1980, pp. 244-245

Studies on the Stability of Vanadyl Chelates with Dithiodiacetic Acid and Diglycollic Acid*

R. K. BAWEJA, S. N. DUBEY** and D. M. PURI

Department of Chemistry, Kurukshetra University, Kurukshetra-132 119, Haryana

Manuscript received 30 June 1979, revised 15 November 1979, accepted 25 December 1979

The proton-ligand stability constants of DTDAA and DGA and the stepwise stability constants of their chelates with VO(IV) have been determined in aqueous medium by potentiometric method at different ionic strengths, (0.1, 0.2 and 0.3*M* $NaClO_4$) and temperatures (25° and 35°). Thermodynamic stability constants and thermodynamic parameters ($\Delta G°$, $\Delta H°$ and $\Delta S°$) have been calculated.

THE survey of the literature reveals that the formation constants of DTDAA and DGA with few metals[1-3] have been reported. However no attempt appears to have been made on the vanadyl chelates with these ligands. The present paper reports the formation of 1 : 1 and 1 : 2 complexes of VO(IV) with the above mentioned ligands.

Experimental

The solutions of DTDAA (Evans' Chematics), DGA (John Baker Inc., Colorado, U. S. A.) and vanadyl sulphate ($VOSO_4 . 2H_2O$ Reachim USSR) were freshly prepared in double distilled water. Perchloric acid (0.04*M*) was prepared by diluting a calculated quantity of the acid with distilled water. Other chemicals used were of A.R. Grade.

Apparatus :

The *p*H measurements were recorded with a Philips *p*H meter (PR9405 M) with glass and calomel electrodes at 25°±0.5° and 35°±0.5° (maintained in a thermostat). The instrument was calibrated using 0.05*M* potassium hydrogen phthalate.

Titration procedure :

The titrations were carried out in a specially designed double walled beaker of the capacity of 250 ml made of pyrex glass using Calvin-Bjerrum[4,5] titration technique as modified by Irving and Rossotti[6]. All the experiments were carried out in an inert atmosphere of nitrogen by bubbling the gas through the solution, during the course of titrations. Titrations were performed in duplicate in order to establish the reproducibility of the measurements.

Results and Discussion

Prootn-ligand stability constants of DTDAA and DGA and the stepwise formation constants of their chelates with vanadyl (IV) were determined using Calvin-Bjerrum technique as modified by Irving and Rossotti. *p*H range investigated for VO (IV)-DTDAA and VO(IV)-DGA systems were 2.25-3.25 and 2.25-3.00 respectively. In the *p*H range mentioned above, factors like hydrolysis of vanadyl ion and the presence of polynuclear species were assumed to be absent, and it is because of :

(i) the departure of the metal chelate titration curve from the ligand titration curve commencing at about *p*H 2.25 which is below the *p*H of hydrolysis of the metal ion, and

(ii) the solutions employed under the experimental conditions were very dilute.

Values obtained at half $\bar{n}_A$ and $\bar{n}$ were further computed using the following techniques[6,7]

(i) Curve-fitting method
(ii) Correction term method
(iii) Pointwise calculation method

The final values of proton-ligand stability constants, log K_1^H and log K_2^H, and metal ligand formation constants, log K_1 and log K_2 are given in Table 1. The thermodynamic stability constants were determined by extrapolating the values to zero ionic strength and the values are given at the bottom of the Table 1.

The thermodynamic parameters ΔG^0, ΔH^0 and ΔS^0 of complexation reactions were calculated at 25° and 35° by using standard equations[8]. The values are tabulated in Table 2.

The values of $\bar{n}$ in the metal-ligand formation curve varies between 0.2 and 1.9, thereby indicating the formation of 1 : 1 and 1 : 2 complexes. A comparison of the stepwise formation constants indicates that the values are slightly higher at 25°

*The paper was presented at the Annual Convention of Chemists, held at Kurukshetra, Sept. 23-27, 1979.
**To whom correspondence may be made.

TABLE 1—PROTON LIGAND STABILITY CONSTANTS OF DTDAA AND DGA AND FORMATION CONSTANTS OF THEIR CHELATES WITH VO(IV)

Ligands used	Ionic concentration (μ)											
	0.1*M*(25°C)			0.2*M*(25°C)			0.3*M*(25°C)			0.1*M*(35°C)		
	$\log K_1^H$	$\log K_2^H$	$\log \beta_2^H$	$\log K_1^H$	$\log K_2^H$	$\log \beta_2^H$	$\log K_1^H$	$\log K_2^H$	$\log \beta_2^H$	$\log K_1^H$	$\log K_2^H$	$\log \beta_2^H$
DTDAA	3.96	2.82	6.78	3.82	2.66	6.48	3.66	2.62	6.28	3.98	2.83	6.81
DGA	4.05	2.63	6.68	3.94	2.49	6.43	3.84	2.42	6.26	4.06	2.64	6.70
	$\log K_1$	$\log K_2$	$\log \beta_2$	$\log K_1$	$\log K_2$	$\log \beta_2$	$\log K_1$	$\log K_2$	$\log \beta_2$	log	$\log K_2$	$\log \beta_2$
DTDAA	2.55	1.53	4.08	2.70	1.70	4.40	2.85	1.85	4.70	2.47	1.51	3.98
DGA	3.10	2.06	5.16	3.18	2.16	5.34	3.30	2.28	5.58	3.02	2.06	5.08

The thermodynamic stability constants $\log K_1^{\mu=0}$ and $\log K^{\mu=0}$ (DTDAA) ; $\log K_1^{\mu=0}$ and $\log K_2^{\mu=0}$ (DGA) were found to be 2.39, 1.37 and 3.01, 1.95 respectively.

TABLE 2—THERMODYNAMIC PARAMETERS OF THE COMPLEXES ($\mu = 0.1M$)

Ligand used	Temp. °C	ΔG_1°	ΔG° (kcal.mole^{-1}) ΔG_2°	ΔG°	ΔH_1°	ΔH° (kcal.mole^{-1}) ΔH_2°	ΔH°	ΔS_1°	ΔS° (cal.mole^{-1}.deg^{-1}) ΔS_2°	ΔS°
	25°	-3.44	-2.07	-5.51						
DTDAA					-3.36	-0.84	-4.20	0.26	4.06	4.32
	35°	-3.48	-2.13	-5.61						
	25°	-4.20	-2.78	-6.98						
DGA					-3.78	-0.00	-3.78	1.38	9.17	10.55
	35°	-4.26	-2.90	-7.16						

as compared to 35° i.e., lower temperature is favourable for complex formation. At a particular ionic strength and temperature the stability order is the same as the order of the basicity of the ligands, i.e., DGA>DTDAA.

Acknowledgement

The authors are thankful to Prof. H. L. Bhatnagar, Head, Chemistry Department, Kurukshetra University, for providing necessary facilities.

References

1. A. SINGH, H. L. KALRA, S. N. DUBEY and D. M. PURI, *Acta Ciencia Indica*, 1977, 3, 209.
2. K. SUZUKI, C. KARAKI, S. MORI and K. YAMASAKI, *J. Inorg. Nuclear Chem.*, 1968, 30, 167.
3. M. CALVIN and K. W. WILSON, *J. Amer. Chem. Soc.*, 1945, 67, 2003.
4. J. BJERRUM, Metal amine formation in aqueous solution, Haase and Son, 1941.
5. H. IRVING and H. S ROSSOTTI, *J. Chem. Soc.*, 1953, 3397.
6. H. M. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.*, 1954, 2904.
7. S. N. DUBEY and R. C. MEHROTRA, *Indian J. Chem.*, 1967, 5, 327.
8. K. B. YATSIMIRSKII and V. P. VASIL'EV, "Instability constants of complex compounds" Pergamon Press, London, P. 59-65.

J. Indian Chem. Soc.,
Vol. LVII, March, 1980, pp. 246-248

Determination of the Composition, Stability Constants and Activation Parameters of UO_2^{2+}-Hexamethylenetetramine Complexes at Dropping Mercury Electrode*

D. RAJENDRA PRASAD† and K. SARASWATHI

Chemistry Department, Sri Venkateswara University, Tirupati-517 502, India

Manuscript received 12 September 1979, accepted 31 December 1979

Polarographic reduction of complexation reactions of hexamethylenetetramine (HMTA) with uranyl ion in 1.0*M* KOAc at dme studied were found to be reversible and diffusion-controlled involving one electron transfer, the slope of log i/i_d -1 vs E plot being 60±2mV. The effect of *p*H on the complex formation was studied and *p*H 4.5 was selected for the study of the present system. Stability constants of the complexes were determined by DeFord and Hume method at different temperatures (25, 30 and 35°) and the activation parameters were also calculated. The mono-dentate HMTA forms tetra co-ordinated complex with UO_2^{2+} ion and the stability constants for different species existing in solution UO_2L^{2+}, $UO_2L_2^{2+}$, $UO_2L_3^{2+}$ and $UO_2L_4^{2+}$ were calculated. The negative of the stability constants for $UO_2L_3^{2+}$ indicates that this species is not existing or highly unstable in solution. The plot of percentage distribution of metal ion present in the form of various species at 25° have also been reported.

RESULTS of an investigation of the electrolytic reduction of the complexes formed by hexamethylenetetramine (HMTA) with some of the metal ions at a mercury dropping electrode in different electrolytes and also at different temperatures were published earlier[1-3]. Though there are many publications dealt with the electrochemical reduction of uranyl ion with some of the amines[4-8], but however the present work describes the detailed study of the complexation reactions of uranyl ion with HMTA as complexing agent and again then stereochemistry of uranyl ion as UO_2-HMTA complexes are going to be similar to some of the metal ions studied earlier with HMTA, say Ni and Cu[2]. Although the reduction of uranyl-amine complexes were found to be a single electron transfer process as was in the case of majority of the earlier literature work[4-8], most of the reports are only the overall stability constants. For the reduction of UO_2-HMTA complexes in 1.0*M* KOAc as supporting electrolyte, reversible one electron transfer prevails over the potential range studied and stability constants and composition of different species formed are investigated at different temperatures.

Experimental

Materials: Uranyl acetate (BDH, AR), Hexamethylenetetramine (Reidel, Germany) were used without further purification. Potassium acetate and triton-X-100 (BDH) lab reagents are used as supporting electrolyte and maximum suppressor respectively. Triply distilled mercury was used as mercury pool.

Instrumentation and methods: The polarographic measurements were made using a manual Toshniwal polarograph type CLO 2A in conjunction with the multiflex galvanometer. The electrolytic cell and the procedure adopted are the same as was described in the earlier papers[1-3]. The half-wave potentials reported here were with respect to the saturated calomel electrode. Before the electrolysis, the experimental solutions prepared with the conductivity water were degassed with purified nitrogen.

Results and Discussion

Effect of pH:

The effect of *p*H on the half-wave potentials of UO_2-HMTA system in 1.0*M* KOAc was studied over a *p*H range of 3.5 to 6.5 and $E_{\frac{1}{2}}$ vs *p*H graph was plotted (Fig. 1). To avoid the hydrolysed product at high *p*H and also to have the half-wave potential shifts to moderately negative values, *p*H 4.5 was selected for the study of the present system.

The polarographic reduction of 1mM UO_2^{2+} ion concentration over the concentration range of HMTA in 1.0*M* KOAc as supporting electrolyte and 0.002% triton-X-100 maxima suppressor, gave

* A part of this work was presented at the Annual Convention of Chemists, 1978 held at Waltair.
† Chemical Laboratory, Central Leather Research Institute, Madras - 600 020.

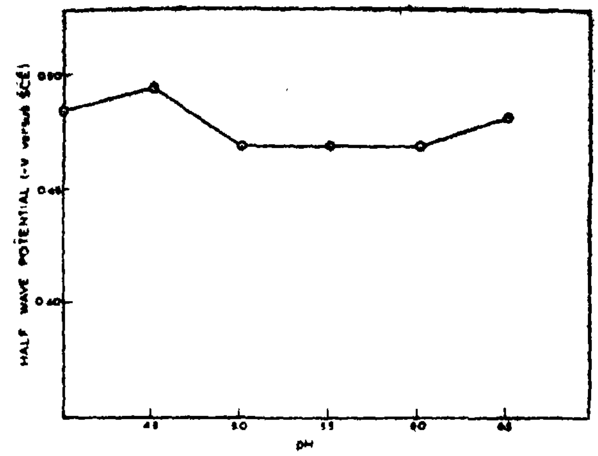


Fig. 1. Plot of pH vs $E_{\frac{1}{2}}$ for UO_2^{2+} -HMTA system at 25°C in 1.0*M* Potassium acetate.

well defined single waves. The reduction of the complexes in each case was a reversible diffusion controlled process and the slopes of the log plots are being 60$\pm$2mV.

Data analysis :

Since the plot of $E_{\frac{1}{2}}$ vs $\log C_x$ is not a linear plot or a smooth curve, but appears to be as many as four segments, therefore the system involves mixture of consecutively formed complex ions but not single final complex species. Hence DeFord and Hume method[9,10] of calculations were applied for evaluation of formation constants of different UO_2-HMTA complexes. The $E_{\frac{1}{2}}$ values as a function of concentration of the ligand were used to calculate $F_0(X)$ function from the equation

$$F_0(X) = \text{Antilog}\,[0.4343(nF/RT)\Delta(E_{\frac{1}{2}}) + \log I_s/I_c]$$

where $F_0(X)$ represents the experimentally measured quantity on the right hand side of the equation. Inorder to determine K_1 to K_n, the graphical extrapolation method devised by Leden[11] was applied. The intercepts of these extrapolated plots correspond to the formation constants values for K_1 to K_n respectively. For verification, the limiting slopes of $F_n(X)$ vs $[X]$ were taken and these values were found to be equal to corresponding K_n. The possible complexes therefore are UO_2L^{2+}, $UO_2L_2^{2+}$, $UO_2L_3^{2+}$ and $UO_2L_4^{2+}$ where L is HMTA and the possible reactions at dme are

In solution **At dme**

$$UO_2^{2+} + HMTA \rightleftharpoons UO_2HMTA)^{2+} \underset{}{\overset{le+Hg}{\rightleftharpoons}} UO^{2}(Hg)^{2+} + HMTA$$

$$UO_2^{2+} + 2HMTA \rightleftharpoons [UO_2(HMTA)_2]^{2+} \overset{le+Hg}{\rightleftharpoons} UO^{2}(Hg)^{2+} + 2HMTA$$

$$UO_2^{2+} + 3HMTA \rightleftharpoons [UO_2(HMTA)_3]^{2+} \overset{le+Hg}{\rightleftharpoons} UO^{2}(Hg)^{2+} + 3HMTA$$

$$UO_2^{2+} + 4HMTA \rightleftharpoons [UO_2(HMTA)_4]^{2+} \overset{le+Hg}{\rightleftharpoons} UO^{2}(Hg)^{2+} + 4HMTA$$

These reduction reactions were carried out at three different temperatures under the identical conditions. From the formation constants data, it is seen that very weak complexes were formed. The trend in increase in the i_d and decrease in formation constant values with increase in temperature were as per the phenomena[8].

Activation Parameters :

The activation parameters have been calculated from the formation constants data at three different temperatures 25, 30 and 35°, substituting in the respective equations

$$\Delta G = -2.303\ RT \log K_{stab}$$

$$\log = K_2/K_1 = [\Delta H(T_2 - T_1)]/4.576T_2T_1$$

and $\Delta S = [\Delta H - \Delta G]/\Delta T$

and these values are summarised in Table 2. The distribution of uranyl ion present in various forms as a function of the ligand concentration was calculated and plotted as percentage distribution *vs* log Cx (Fig. 2). The experimental data is tabulated

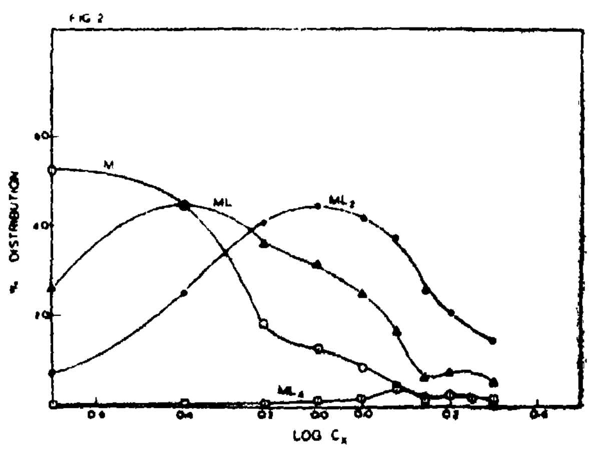


Fig. 2. Percentage Distribution of metal ion as different species vs logarthamic concentration of HMTA at 25° in 1.0*M* Potassium acetate.

TABLE 1a—POLAROGRAPHIC DATA AND ANALYSIS OF F_n (X) VALUES FOR THE UO_2^{2+}-HMTA SYSTEM IN KOAc MEDIUM AT 25, 30 AND 35°C (pH 4.5)

HMTA	25°C			30°C			35°C		
	i_d (μA)	$-E_{\frac{1}{2}}$ V vs SCE	F_o(X)	i_d (μA)	$-E_{\frac{1}{2}}$ V vs SCE	F_o(X)	i_d (μA)	$-E_{\frac{1}{2}}$ V vs SCE	F_o(X)
M									
0.00	10.760	0.475	1.00	12.300	0.476	1.00	14.640	0.482	1.00
0.20	9.374	0.488	1.91	11.500	0.478	1.88	12.160	0.496	2.04
0.40	9.305	0.492	2.25	10.470	0.492	2.10	12.890	0.499	2.16
0.80	7.615	0.510	5.53	8.642	0.510	5.24	10.540	0.514	4.64
1.00	6.372	0.515	7.07	7.762	0.515	7.86	8.933	0.523	7.70
1.20	5.705	0.524	12.12	7.615	0.524	10.18	8.790	0.532	11.00
1.60	5.056	0.537	24.00	6.298	0.540	12.74	6.884	0.542	20.46
1.80	4.834	0.565	74.46	5.056	0.558	56.53	6.446	0.568	58.29
2.00	3.552	0.566	67.61	3.955	0.573	128.30	4.834	0.560	57.48
2.20	3.076	0.566	121.60	3.662	0.574	144.10	5.126	0.569	76 08
2.40	3.076	0.578	194.30	2.783	0.578	169.00	4.909	0.582	129.80

TABLE 1b—SUMMARISED STABILITY CONSTANTS DATA OF DIFFERENT SPECIES AT DIFFERENT TEMPERATURES

Complex species	Stability constants at 25°C	30°C	35°C
UO_2L^{2+}	2.50	2.00	1.75
$UO_2L_2^{2+}$	3.80	3.30	2.50
$UO_2L_3^{2+}$	-1.14	-1.30	-0.58
$UO_2L_4^{2+}$	1.25	1.13	1.01

TABLE 2—ACTIVATION PARAMETERS FOR UO_2^{2+}-HMTA SYSTEM

Temperature °C	ΔG(Kcal)	ΔH(Kcal)	ΔS(cal/Deg./Mole)
25	-0.013	-	-
30	-0.007	-3.622	-12.02
35	-0.0006	-4.164	-13.62

in Table 1. The negative values of the stability constants of $UO_2L_3^{2+}$ at different temperatures indicates that this species is not existing or highly unstable in solution. The variation in the stability constant values at different temperatures apart from the above mentioned factors might be accounted from the entropy change, steric and electrostatic effects in addition to the statistical considerations.

References

1. K. SARASWATHI and D. RAJENDRA PRASAD, *Indian J. Chem.*, 1977, **15A**, 251.
2. K. SARASWATHI and D. RAJENDRA PRASAD, *Indian J. Chem.*, 1977, **15A**, 842.
3. D. RAJENDRA PRASAD and K. SARASWATHI, *Indian J. Chem.*, 1978, **16A**, 242.
4. TSAI-TEH LAI and HAN-TOUG LIN, *J. Chinese Chem. Soc., SerII*, 1963, **10**, 71.
5. R. N. SHEHELOKOV, I. M. SHUL'gina and I. I. Chernyaev, *Zh. Neorg. Khim.*, 1967, **12**, 1246.
6. A. L. J. RAO and B. K. PURI, *Fresenius Z. Anal. Chem.*, 1971, **225**, 20.
7. S. A. MERKUSHEVA, N. A. SHORIK and V. V. SEREBRENNIKOV, *Radiokhimiya*, 1968, **10**, 591.
8. D. P. JOSHI and LAL KEEMTI, *J. Indian Chem. Soc.*, 1969, **46**, 484.
9. D. D. DEFORD and D. N. HUME, *J. Amer. Chem. Soc.*, 1951, **73**, 5321.
10. D. D. DEFORD and D. N. HUME, *J. Amer. Chem. Soc.*, 1951, **73**, 5323.
11. I. LEDEN, *Z. Phys. Chem.*, 1964, **188**, 160.

J. Indian Chem. Soc.,
Vol. LVII, March 1980, pp. 249-251

Rare Earth Complexes with N, O-Donor Ligands. Part-I. Nitrato-Complexes of Terpositive Yttrium and Lighter Lanthanides with 2-(2′-Hydroxyphenyl) Benzimidazole

A. MISHRA*, M. P. SINGH and J. P. SINGH

Chemical Laboratory, Bhagalpur University, Bhagalpur-812 007

Manuscript received 27 August 1979, accepted 20 December 1979

The 8-coordinate complexes of the type $[M(HO\text{-}PhBzH)_2(NO_3)_2]NO_3.nH_2O$ (M = Y, La, Ce, Pr, Nd, Sm; n = 0.5 – 4; HO-PhBzH = 2-(2′-hydroxyphenyl) benzimidazole) separate in the solid state when the metal nitrates interact with the ligand in hot ethyl acetate. Complexes have been characterised by elemental analyses, magnetic susceptibility measurements and electrical conductance values. Infrared spectra reveal the presence of both coordinated (C_{2v}) and uncoordinated (D_{3h}) nitrate groups. The electronic spectra of Pr(III)-, Nd(III)-, and Sm(III)-complexes have been analysed in terms of LSJ levels.

2-(2′-Hydroxyphenyl) benzimidazole (HO-Ph-BzH) is a potent bidentate N,O-donor ligand forming a six-membered chelate ring using the phenolic O and the tertiary N of the imidazole ring. Harkins *et al*[1]. isolated complexes of the type $M(O\text{-}PhBzH)_2$ with Co(II), Cu(II), and Zn(II), either from neutral or slightly basic (pH ~ 8) solution. We report here the nitrato-complexes of Y(III), La(III), Ce(III), Pr(III), Nd(III) and Sm(III).

Experimental

Materials: 2-(2′-Hydroxyphenyl) benzimidazole was prepared as described in literature[2]. Nitrates of La(99.99%), Ce(99.9%), Pr(99.99%), Nd(99.99%), Sm(99.99%) and Y(99.99%), obtained as hydrated crystals from the Indian Rare Earths, were used as such.

Preparation of Complexes: The metal nitrates and the ligand in 1 : 2 molar proportion, dissolved separately in hot ethyl acetate, were mixed and refluxed on steam-bath for about 15 minutes, after which the separation of the solid started. The ease of separation increased with increasing atomic number of the metal. It was further refluxed for 30-60 minutes in order to increase the particle size of the solid. The solid was filtered, washed thoroughly with hot ethyl acetate and dried over $CaCl_2$.

Physical Measurements: A Philips resistance bridge, model PR 9500, was employed to determine the electrical conductances in solution. Magnetic susceptibility measurements were made using Kahn Faraday balance, calibrated[3] with $Hg[Co(NCS)_4]$, Pascal's constants[4] having been used for making diamagnetic corrections. Infrared spectra were recorded using Beckman IR-12 spectrophotometer in KBr discs through commercial services of the Regional Sophisticated Instrumentation Centre, IIT, Madras. Electronic spectra were scanned on Cary 14 ratio-recording spectrophotometer using matched 10 mm silica cells.

Results and Discussion

The terpositive yttrium and the lighter lanthanide nitrates uniformly form the 8-coordinate dinitrato-*bis*-chelates of the general formula $[M(HO\text{-}PhBzH)_2(NO_3)_2]NO_3.nH_2O$ (n = 0.5 – 4), supported by the electrical conductance values of 103-137 $ohm^{-1}\ cm^2\ mole^{-1}$ in DMF at 304°K (Table 1). The presence of lattice water in each case is ascertained by recording the loss in weight on heating upto 120° and observing no loss on further heating upto 180°.

The room-temperature magnetic moment values of Ce^{III} (2.74 BM), Pr^{III} (3.57 BM), and Nd^{III} (3.68 BM), having $^2F_{5/2}$, $^3H_4$, and $^4I_{9/2}$ ground state terms, respectively, correspond to the formula[5]: $\mu_{eff} = g[J(J+1)]^{\frac{1}{2}}$. However, the value of 1.75 BM observed for Sm^{III} ($^6H_{5/2}$) as against the calculated value of 0.84 BM suggests a considerable population of the excited J-levels of the metal ion[5].

Infrared Spectra:

An *uncoordinated nitrate* (D_{3h}) is expected to show three IR-active fundamentals[6], $\nu_2(A_2'')$: 831 cm^{-1}, $\nu_3(E')$: 1390 cm^{-1}, $\nu_4(E')$: 790 cm^{-1}, whereas

*For Correspondence

TABLE 1—STOICHIOMETRY, ELECTRICAL CONDUCTANCES (OHM^{-1} CM^{2} MOLE^{-1}, DMF) AND MAGNETIC MOMENTS (B.M.)

Complex	%M	%N	%loss in wt. 120°C*	Cond. 304°K	μ_{eff} 298°K
$[LaX]NO_3 \cdot 1.5H_2O$	R 17.98	12.69	3.40	137	—
	F 18.15	12.52	3.60		
$[CeX]NO_3 \cdot 4H_2O$	R 17.11	11.97	8.79	127	2.74
	F 16.95	12.00	8.40	—	
$[PrX]NO_3 \cdot 1.5H_2O$	R 18.17	12.66	3.48	127	3.57
	F 18.16	12.06	3.47		
$[NdX]NO_3 \cdot 2.5H_2O$	R 18.12	12.32	5.80	132	3.68
	F 18.08	12.01	5.54		
$[SmX]NO_3 \cdot 0.5H_2O$**	R 19.63	12.80	1.10	118	1.75
	F 19.35	12.90	1.50		
$[YX]NO_3 \cdot 2.5H_2O$	R 12.00	13.29	***	103	—
	F 12.46	12.82			

$X = (HO\text{-}PhBzH)_2^{+}(NO_3)_2^{-}$; $HO\text{-}PhBzH = C_{15}H_{10}N_2O$; *No further loss upto 180°C

***Could not be done on account of low yield.

**	%C	%H
Found :	41.12	2.87
Reqd. :	40.77	2.76

a *coordinated nitrate* (C_{2v}) exhibits six such fundamentals[6], $\nu_4(B_1)$: 1530-1480 cm^{-1}, $\nu_1(A_1)$: 1290 cm^{-1}, $\nu_2(A_1)$: 1030 cm^{-1}, $\nu_6(B_2)$: 810 cm^{-1}, $\nu_3(A_1)$: 740 cm^{-1} and $\nu_5(B_1)$: 713 cm^{-1}.

The $\nu_4(B_1)$ mode in each complex appears as a doublet or a multiplet in the region 1420-1485 cm^{-1}, and the $\nu_1(A_1)$ mode falls in the range 1255-1315 cm^{-1}. The magnitude of ν_4-ν_1 ranges from 160 to 215 cm^{-1} in these complexes, which might be considered to be in favour of the bidentate character of the C_{2v}-nitrate[7], though this has not been considered as a good criterion to distinguish between a bidentate and a monodentate nitrate by Topping[8] and Kawano *et al.*[9] However, the X-ray investigations reveal that the nitrate group behaves as a bidentate ligand in the nitrato-complexes of Ce(III)[10], UO_2(II)[11], and Th(IV)[12] and it was proposed by Cousins and Hart[13] that, in general, nitrate exhibits a bidentate character when coordinated to the lanthanide ions. Thus we assume that in the present complexes too the nitrate groups are bidentate.

The weak bands near 1010-1035 cm^{-1} are assigned to the $\nu_2(A_1)$ mode, those in the region 790-815 cm^{-1} to the $\nu_6(B_2)$ mode and similar ones at 690-730 cm^{-1} to the $\nu_5(B_1)$ mode of C_{2v}-nitrate.

The $\nu_3(E')$ bands in the range 1345-1383 cm^{-1} and $\nu_2(A'')$ ones in the region 835-860 cm^{-1} ascertain the presence of D_{3h}-nitrate.

Harkins *et al.*[1] assigned the broad absorption band centered at 2530 cm^{-1} to the strongly H-bonded phenolic OH. However, we propose that the strong doublet at 3210, 3280 cm^{-1} may be ascribed to phenolic OH. There is only a broad shoulder at 2530 cm^{-1}, whereas the 3200-3300 cm^{-1} bands are prominant ones, which are broadened and intensified in complexes containing water of crystallisation. As H-bonding lowers the stretching frequency of free phenolic OH, a lowering in ν(NH) may also be expected and thus we propose to assign the medium intensity band of the ligand at 3030 cm^{-1} to ν(NH) instead of the one at 3155 cm^{-1} as proposed by Harkins *et al.*[1] On account of the presence of water of crystallisation in each complex, the 3030 cm^{-1} band is converted, with a slight shift, into a shoulder on OH stretching bands at 3100-3500 cm^{-1}. The δ(HOH) manifests mainly as a set of shoulders in the range 1615-1665 cm^{-1}.

Electronic Spectra :

The spectrum of the sulphur-yellow Ce(terpyridyl)$^{3+}$, recorded by Sinha[14], showed a strong absorption near 401 nm, which was attributed to $4f \rightarrow 5d$ transition. A strong and continuous absorption from 450 nm towards ultraviolet by the sulphur-yellow Ce(III)-complex of HO-PhBzH in DMF also suggests a similar transition.

The spectral results for Pr(III)-, Nd(III)-, and Sm(III)-complexes in DMF have been analysed. The extent of red-shift observed in $^3P_2$, $^3P_1$, $^3P_0$ and $^1D_2$ bands of Pr(III) in the complex in the comparison to those of the free-ion[15] or the aquo-ion[16,17] suggests a very negligible nephelauxetic effect produced by HO-PhBzH. Beyond 700 nm, the levels $^1G_4$, $^3F_4$, $^3F_3$, and $^3F_2$ have been located, which have not been reported previously in the aquo-ion[16,17] or the terpyridyl-complex[14]. Numerous bands in the region 5620-6390 cm^{-1} remain unassigned at present.

Only a little red-shift observed in the spectral bands of Nd(III) in this complex with respect to the calculated values[18,19] or those of the aquo-ion[16,17,20] suggests a negligible nephelauxetic effect produced by this ligand. An idea of the extent of the nephelauxetic effect may be obtained[21] from the shift in the transition $^4I_{9/2} \rightarrow {}^2P_{1/2}$, which, however, is obscured in the present system by charge-transfer band in the same region.

A comparison of the calculated values of J-levels of Sm^{3+} in $LaCl_3$-host[22] with those observed in the complex under study leads to the assignment of the levels $^6H_{13/2}$, $^6F_{5/2}$, $^6F_{7/2}$, $^6F_{9/2}$, and $^6F_{11/2}$. Numerous bands appear in the region 15820-23870 cm^{-1}, which have not been assigned at present. The ^6P level, which was located by Sinha[14] in Sm(III)-terpridyl system at 24780 cm^{-1} is obscured by the charge-transfer band in the present case.

Acknowledgement

The authors thank the University Grants Commission, New Delhi, for financial support. They also thank Professor B. M. Shukla and Professor R. C. Aggarwal of the Banaras Hindu University, Varanasi, for some spectral and magnetic measurements.

References

1. T. R. Harkins, J. L. Walter, O. E. Harris and H. Freiser, *J. Amer. Chem. Soc.*, 1956, **78**, 260.
2. J. L. Walter and H. Freiser, *Anal. Chem.*, 1953, **25**, 127.
3. B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 1958, 4190.
4. B. N. Figgis and J. Lewis, 'Modern Coordination Chemistry' edited by J. Lewis and R. G. Wilkins, Interscience, New York, 1967, p. 403.
5. S. P. Sinha, 'Complexes of the Rare Earths', Pergamon Press, New York, 1966, p. 14.
6. J. H. Forsberg, *Coord. Chem. Rev.*, 1973, **10**, 208.
7. K. Nakamoto, 'Infrared and Raman Spectra of Inorganic and Coordination Compounds', Wiley Interscience, New York, 1978, p. 246.
8. G. Topping, *Spectrochim. Acta*, 1965, **21**, 1743.
9. Y. Kawano and V. K. L. Osorio, *J. Inorg. Nuclear Chem.*, 1977, **39**, 701.
10. M. D. Lind, B. Lee and J. L. Hoard, *J. Amer. Chem. Soc.*, 1965, **87**, 1111.
11. J. E. Fleming and H. Lynton, *Chem. Ind.*, 1960, 1415.
12. T. Ucki, A. Zalkin and D. H. Temphton, *Acta Cryst.*, 1966, **20**, 836.
13. D. R. Cousins and F. A. Hart, *J. Inorg. Nuclear Chem.*, 1967, **29**, 1745.
14. S. P. Sinha, *Z. Naturforsch.*, 1965, **20a**, 552.
15. S. P. Sinha, 'Complexes of the Rare Earths', Pergamon Press, New York, 1966, p. 97.
16. S. Misumi, S. Kida, T. Isobe and A. Inazumi, *Bull. Chem. Soc. Japan*, 1968, **41**, 25.
17. S. Misumi, S. Kida and M. Aihara, *Coord. Chem. Rev.*, 1968, 3, 193.
18. B. G. Wybourne, *J. Chem. Phys.*, 1960, **32**, 639.
19. J. C. Eisenstein, *J. Chem. Phys.*, 1963, **39**, 2134.
20. S. P. Sinha, *J. Inorg. Nuclear Chem.*, 1965, **27**, 115.
21. S. P. Sinha, 'Complexes of the Rare Earths', Pergamon Press 'New York, 1966, p. 106.
22. S. P. Sinha, 'Complexes of the Rare Earths', Pergamon Press, New York, 1966, p. 109.

J. Indian Chem. Soc.,
Vol. LVII, March 1980, pp. 252-254

Transition Metal Complexes of Heterocyclic Ligands. Part-II. Complexes of Some Schiff's Bases Derived from 2-furan Carboxaldehyde and Aromatic Amines

(Mrs.) P. R. SHUKLA and (Miss) RENU TAKRU

Chemistry Department, Lucknow University, Lucknow

Manuscript received 21 May 1979, accepted 30 December 1979

The compound 2-furan carboxaldehyde reacts with aromatic amines such as aniline, *m*- and *p*- toluidines to form schiff's Sbases (A) which function as bidentate ligands *in situ*, using the oxygen atom of furan ring and the imino nitrogen as the bonding sites, giving crystalline complexes of type $[Cu(H_2O)_2A]SO_4$ and $[Ni(H_2O)_4A]SO_4$. These have been assigned planar and octahedral structures respectively on the basis of analytical, magnetic and spectroscopic data. A calculation of the ligand field parameters has also been made.

AN extensive amount of work has been done on the Schiff's base complexes of transition elements, prepared by using a variety of aldehydes and amines. Almost no work has been reported on the Schiff's base complexes of 2-furan carboxaldehyde, although the free Schiff's bases formed between furfural or its derivatives and some arylamines have been studied thermo kinetically and qualitatively[1-5]. In a previous communication we had reported complexes of free furfural with some metal(II) sulphates[6]. The present paper reports the preparation of six complexes of furfuraldimines with copper(II) and nickel(II) sulphates. The complexes have been fully characterised and their structures determined as outlined below.

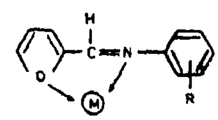
Experimental

The complexes have been prepared *in situ* by mixing an equivalent amount of furfural (1 mole) and amine (1 mole), in methanol under stirring. A red coloured solution was obtained to which an calculated amount of metal(II) sulphate was added and the reaction mixture was further stirred for 8 hours. Heating makes the solution viscous and hence the stirring was done at room temperature. At the end of the period a crystalline complex was obtained, which was filtered, washed, dried and analysed.

The conductivities were measured on a Philips PR9500 magic eye type instrument. The magnetic moments were obtained by Gouy's method and the electronic spectra were measured in the form of solid samples on a VSU-2P spectrophotometer in the range 200-1400 nm.

Discussion

The Schiff's bases (A) prepared in the investigation are proposed to have the following structure



(A)

R = H, m—CH_3 or p—CH_3

and it is thus expected that coordination should take place from furan oxygen as well as azomethine link. The ligand is therefore bidentate in nature and should occupy any two adjacent positions in the coordination geometry of metal(II) ion.

The reaction with the ligand takes place only *in situ* and the parent Cu(II) & Ni(II) SO_4 which contain four and six coordinated water molecules are found to lose only two of these, irrespective of the time of reaction. Only one molecule of ligand is thus added and the other coordination sites are still occupied by water molecules.

Results of similar type were obtained during the studies on the ligand replacement reactions of some metal(II) sulphate complexes. Addition of ligands like aromatic amines, thiourea or furfural itself, led to the replacement of two water molecules, while the others could only be replaced by using stronger ligands like chelating diamines[6-8]. The analytical data of the present complexes (A) confirm that only one Schiff's base molecule has been added, and the other water molecules remain still attached to the metal.

The molar conductances of complexes (table 1) show that these behave as 1 : 1 electrolytes and hence the sulphate ion is not coordinated. The molecular formulae of the complexes are thus $[Cu(H_2O)_2A]SO_4$ and $[Ni(H_2(H_2O)_4]A\ SO_4$.

copper(II) and nickel(II) complexes in planar and octahedral environments respectively.

The diffuse reflectance spectra of all the complexes show one sharp band around 34.50 kK

TABLE 1—ANALYTICAL, MOLAR CONDUCTANCE AND MAGNETIC MOMENT DATA

Complex no.	Complex	% metal	%C	%H	%N	$\%SO_4$	mhos	in B.M
1.	$Cu(H_2O)_2(C_{11}H_9NO)\ SO_4$	17.26 (17.31)	36.25 (36.01)	3.62 (3.57)	3.45 (3.82)	26.90 (26.19)	305.6	1.856
2.	$Ni(H_2O)_4(C_{11}H_9NO)\ SO_4$	14.82 (14.75)	32.96 (33.19)	3.15 (3.29)	3.62 (3.52)	24.84 (24.13)	312.6	3.452
3.	$Cu(H_2O)_2(m\text{-}C_{12}H_{11}NO)\ SO_4$	16.45 (16.68)	37.50 (37.84)	3.72 (3.97)	3.86 (3.68)	25.01 (25.22)	302.8	1.872
4.	$Ni(H_2O)_4(m\text{-}C_{12}H_{11}NO)\ SO_4$	14.05 (14.28)	34.86 (34.96)	3.95 (3.70)	3.46 (3.40)	23.21 (23.32)	310.5	3.483
5.	$Cu(H_2O)_2(p\text{-}C_{12}H_{11}NO)\ SO_4$	16.28 (16.68)	37.62 (37.84)	3.75 (3.97)	3.40 (3.68)	25.62 (25.72)	—	1.842
6.	$Ni(H_2O)_4(p\text{-}C_{12}H_{11}NO)\ SO_4$	14.10 (14.28)	34.56 (34.96)	3.72 (3.68)	3.60 (3.39)	23.59 (23.31)	307.0	3.043

TABLE 2—ELECTRONIC SPECTRAL DATA

Complex no.	Copper(II) complexes in nm	Energy in kK	Dq in cm^{-1}	Nickel(II) complexes V_1 in kK	V_2 in kK	V_3 in kK	Dq in kK	in cm^{-1}
1.	760	13.16	1316	—	—	—	—	—
2.	—	—	—	919.1	13.51 12.82	25.00	919.1	947.9
3.	762	13.05	1305	—	—	—	—	—
4.	—	—	—	917.7	13.68 12.34	24.75	917.7	934.5
5.	770	12.98	1299	—	—	—	—	—
6.	—	—	—	9.132	13.88 12.34	25.02	913.2	904.2

In the infra red spectra of complexes (a) a strong broad band appears around 3410 cm^{-1} assigned as the OH stretching and its negative shift is an indication of the coordination of water molecule[9].

(b) Another very sharp and strong band is seen at 1630±10 cm^{-1} in all the complexes. This is the azomethine stretch, which in free ligand occurs at around 1600 cm^{-1}. This positive shift shows that its nitrogen atom is involved in coordination as found for many other Schiff's base complexes[10-11].

(c) Sharp bands at 1125±5 and 630±10 cm^{-1} are due to the V_3 & V_4 modes of uncoordinated sulphate ion.

(d) A very sharp band at 500±10 cm^{-1}, is clearly observed, which is the band involving the metal and furan oxygen[12-13].

These data confirm the molecular formulae of the complexes mentioned earlier. The magnetic moments of the complexes are in the usual range of one and two unpaired electrons as expected for

and another weak one at 22.75 kK. These bands have been observed in the spectra of many other Schiff's bases as well as their complexes[14-15]. The former corresponds to the perturbed benzene ring transition of amine fragment and later is due to the whole aromatic ring oriented trans with respect to double bond. There is an additional very broad band present in the spectra, the maximum for which has been approximated to lie around 1300 kK. This is the characteristic d-d transition of copper(II) in planar environment[15], as the tetrahedral complexes usually give bands in the region lower than 10.00 kK[16,17]. The broadness of the band is probably due to the presence of different ligands around the metal, which produce a ligand field of sufficiently low symmetry in complexes, thus causing severe distortion from the usual planar structure. The 10 Dq values for the complexes lie in the range 12,987-13,160 cm^{-1} as expected for their planar geometry.

The nickel(II) complexes exhibit three transitions V_1, V_2 & V_3 characteristic of octahedral structure[18,19]. These are seen around 9.20 ; 13.60 and 25.00 kK. The V_2 transition is broad and splits

into two components. This is a familiar phenomenon in such nickel(II) complexes which show distortions from octahedral structures due to the presence of dissimilar ligands in coordination sphere[20].

The V_1 transition is directly equal to Dq which comes around 920.0 cm^{-1} in the complexes, while the B values are around 925.0 cm^{-1}. These values are typical of distorted octahedral complexes of nickel(II)[20,21].

The Dq values of the parent ions i.e., $[Cu(H_2O)_4]^{2+}$ and $[Ni(H_2O)_6]^{2+}$ are 1250 and 890 cm^{-1}. It thus appears that in these complexes, a ligand field of only slightly greater magnitude is being produced or the bidentate Schiff's base is only a moderately strong ligand than the water molecules. Hence it can be seen why only some of the water molecules and not all are being replaced, to give the complexes of type reported here.

Acknowledgement

One of us (RT) is thankful to State Council of Science and Technology, U.P., for financial assistance.

References

1. J. S. Sandhu, Suresh Mohan and P. S. Sethi, *J. Indian Chem. Soc.*, 1971, **48**, 693.
2. J.S. Sandhu, Suresh Mohan and P. S. Sethi, *J. Indian Chem. Soc.*, 1971, **48**, 697.
3. I. K. Tovmasyan, N. Ya. Avdeev, N. I. Lyutkin, E. P. Khanin, G. F. Sokol, L. F. Issled Yatsenko, *Thermograju Karroz*, 1970, **22**, 73.
4. N. I. Lyutkin, *Issled. Thermograju-Korroz*, 1970, 37.
5. F. Khotz and A. Zinke, *Sci. Pharm.*, 1958, **26**, 191.
6. P. R. Shukla and R. Takru, *Curr. Sci.*, Under publication.
7. P. R. Shukla, Neelam Verma, *Indian J. Chem.*, 1978, **16**, 810.
8. P. R. Shukla and Neelam Verma, *Indian J. Chem.*, Under publication.
9. R. H. Prince and D. A. Stotter, *Inorg. Chimica. Acta*, 1974, **10**, 89.
10. J. E. Covacic, *Spectrochim. Acta*, 1967, **23A**, 183.
11. P. Ebyssi and J. J. Charette, *Spectrochim. Acta*, 1967, **19**, 1407.
12. R. J. Niedzielski and Zaiderc, *Canad. J. Chem.*, 1965, **213**, 1618.
13. H. K. Hall and R. Zbinden, *J. Amer. Chem. Soc.*, 1958, **80**, 6428.
14. V. J. Minkiu, O. A. Osipov and V. A. Kogan, R. R. Shagiduchima, R. L. Terente'ev and O. A. Rasvskii, *Russ. J. Phys. Chem.*, 1964, **38**, 938.
15. L. E. Orgel, *J. Chem. Phys.*, 1956, **23**, 5.
16. R. H. Holm, A. Chakravarty and L. J. Theriot, *Inorg. Chem.*, 1966, **5**, 625.
17. A. Chakravarty and T. S. Kauvan, *J. Inorg. Nuclear Chem.*, 1967, **29**, 1691.
18. W. C. Fernelius and W. Manch, *J. Chem. Educ.*, 1961, **38**, 192.
19. J. Michael and R. A. Walton, *J. Inorg. Nuclear Chem.*, 1975, **37**, 71.
20. C. K. Jorgenson, *Acta. Chim. Scand*, 1955, **9**, 116.
21. C. H. Faye and J.L. Horwood, *Canad. J. Chem.*, 1967, **45**, 2335.

J. Indian Chem. Soc.,
Vol. LVII, March 1980, pp. 255-258

Oxovanadium(IV) Complexes with Thiohydrazide Derivatives

(Mrs.) URMILA KUMARI, C. P. SINGH and L. K. MISHRA*

Department of Chemistry, Patna University, Patna-800 005

Manuscript received 23 October 1979, accepted 30 December 1979

The complexes of oxovanadium(IV) with phenylthiohydrazide (pth), furfurylthiohydrazide (fth), *p*-anisidyl-thiohydrazide (*p*-anth) and salicylthiohydrazide (H_3Salth) of the formulae $VOL_2SO_4.nH_2O$ (where L = pth, fth or *p*-anth and n = 0 or 1), $VO(H_3Salth)SO_4.CH_3OH$, $VO(Salth)B.3CH_3OH$ (B = pyridine or β-picoline) and $VO(Salth).4CH_3OH$ have been prepared and characterised by electronic reflectance, infrared and magnetic susceptibility measurements.

THE complexes of oxovanadium (IV) and a number of other metals with acylhydrazides and acylhydrazones have been studied in detail[1-4]. Relatively a little is known about the complexes of metal ions with acylthiohydrazides[5]. Jensen and Miquel[6] had reported that phenylthiohydrazide forms nickel (II) chelates of the same types as are formed by thiosemicarbazides[7]. Recently Dilwonth *et al.*[8] have reported a number of molybdenum (III) complexes with thiohydrazides and thiohydrazones. The complexes of oxovanadium (IV) and various other metal ions with acylthiohydrazides have not been reported hitherto. In present communication, we are reporting the complexes of oxovanadium (IV) acylthiohydrazides (L).

$$\mathrm{R{-}C({=}S){-}NH{-}NH_2}$$

(R = phenyl, *p*-anisidyl, furfuryl and *o*-hydroxyphenyl groups)

Experimental

The ligands were prepared as reported in literature[9] and vanadyl sulphate tetrahydrate and vanadyl chloride used were BDH AR grade chemicals.

Preparation of the complexes :

$VOL_2SO_4.nH_2O$: (L = pth, fth or *p*-anth and n=0 or 1).

These complexes were obtained as dark violet or dark brown precipitates when a methanolic solution of hydrated vanadyl sulphate (1.2 g in 30 ml) was treated with 1 : 2 molar proportion of appropriate ligand dissolved in minimum volume of methanol. In case of furfurylthiohydrazide, the complex was separated on adding equal volume of ether to the resulting solution of the complex. The complexes were collected on a filter, washed with methanol and ether and dried in a vacuum desiccator over $CaCl_2$.

$VO(H_3Salth)\ SO_4.\ CH_3OH$:

Hydrated vanadyl sulphate, $VOSO_4.4H_2O$ (1.2g) was dissolved in 30-40 ml of methanol and treated with a methanolic solution salicylthiohydrazide (0.9 g, about 1 : 1 molar ratio) when a deep violet solution resulted. From the resulting solution, a dark violet complex separated out slowly. The product was collected on a filter and dried as above.

$VO(Salth)B.\ 3CH_3OH$: (B = pyridine or β-picoline).

About 1.2 g of $VOSO_4.\ 4H_2O$ was dissolved in 30 ml of methanol and 4-5 ml of pyridine (or β-picoline). The resulting yellowish green solution was treated with 0.9 g of ligand (about 1 : 1 molar ratio) dissolved in the same solvent. From the resulting dark violet solution, an almost black insoluble product separated out immediately. The product was collected on a filter, washed with methanol and dried in air.

$VO(Salth).\ 4CH_3OH$:

About 1.0 g of vanadyl chloride was dissolved in 30-40 ml of methanol and treated with the ligand in 1 : 1 molar ratio. The *p*H of the resulting dark violet solution was raised to 7-8 by adding methanolic solution of sodium acetate when almost black complex separated out. The product was filtered, washed and dried as above.

The elemental analyses, room temperature magnetic moment values and spectral band positions of the complexes are recorded in Table 1.

The magnetic susceptibility and electronic reflectance spectra of the complexes were recorded as reported earlier[10]. The IR spectra of the complexes were recorded on Perkin Elmer 577 spectrophotometer as KBr disc. The prominent IR bands are recorded in Table 2.

Results and Discussion

On the basis of analytical results, the empirical formulae of the complexes are given in Table 1. Excepting salicylthiohydrazide, the other thiohydrazides appear to be bonded as bidentate neutral ligands in complexes $VOL_2SO_4 \cdot nH_2O$ (L = pth, fth or *p*–anth). Salicylthiohydrazide is bonded as a neutral molecule in complex VO (H_2Salth) SO_4. CH_3OH and as a dibasic acidic molecule in other complexes. Salicylthiohydrazide complexes are almost insoluble in ethanol or water but slightly dissolve in DMF. The poor solubility of the complexes indicates their polymeric nature.

The sulphato complexes $VOL_2SO_4 \cdot nH_2O$ (L = pth, fth or *p*—anth and n = O or 1) and VO(H_2 Salth) SO_4. CH_3OH display magnetic moment values between 1.78-1.92 BM, expected for one unpaired spin. The other oxovanadium (IV) complexes, VO (Salth)B. $3CH_3OH$ (B = pyridine or β-picoline) and VO (Salth)$4CH_3OH$ show subnormal magnetic moment values (μ_{eff} 1.34–1.54 BM) similar to dinuclear oxovanadium (IV) complexes[11,12].

These complexes exhibit two to three medium to weak broad bands or shoulder in the region 26,000—14,000 cm^{-1}. The electronic spectral pattern of the complexes is compatible with electronic spectra of six coordinated oxovanadium (IV) complexes[13,14]. (The spectral band positions with their assignments are shown in Table 1).

The IR spectra of the complexes display V = O stretching vibration as strong band in the region 970-980 cm^{-1} (Table 2). In case of bischelated complexes, $VOL_2SO_4 \cdot nH_2O$, the ν (V=O) vibration is sharp while in other complexes, it is strong and broad indicating their di or polynuclear nature. In these vanadyl complexes, the ν(V = O) vibration occurs in the same region suggesting that dimerisation or polymerisation in the complexes does not take place through V = O oxygen[15].

The ν (V = O) vibration is not affected in band position in pyridino/picoline complexes indicating that pyridine/picoline does not occupy V = O axial position[16].

Free thiohydrazides display strong and distinct NH_2 and N-H stretching vibrations in the region 3300-3100 cm^{-1}. In complexes, these bands are observed as only one broad and medium band between 3350 and 3100 cm^{-1}. The NH_2 deformation vibration of the ligand is slightly shifted to lower frequencies in almost all vanadyl complex. Thus, it is inferred that the terminal nitrogen atom of thiohydrazide group is one bonding site of ligand in the complexes[16]. These ligands possess potential thioamide group and therefore display characteristic thioamide bands in the region 1550-700 cm^{-1}. (The shift of thioamide bands in the complexes are shown in Table 2). The thioamide band IV due to ν(C=S) is shifted to lower frequency by 10-30 cm^{-1} in sulphato complexes while in

TABLE—1

Complex	Colour	% M Found (Reqd)	% N Found (Reqd)	% C Found (Reqd)	% H Found (Reqd)	% SO_4 Found (Reqd)	μ_{eff} (BM)	Spectral band position cm^{-1} (nm)	Assignments
VO(pth)$_2SO_4$	Dark brown	10.81 (10.94)	12.06 (11.99)	36.11 (35.97)	3.57 (3.45)	20.34 (20.55)	1.86	17260m (580)	$b_2—e_\pi^*$
								19680 sh (510)	$b_2—b_1^*$
								23260 m (430)	$b_2—a_1^*$ + C—T
VO(fth)$_2SO_4$	Dark violet	11.44 (11.39)	12.62 (12.52)	27.01 (26.85)	2.81 (2.70)	20.98 (21.47)	1.88		
VO(*p*-anth)$_2SO_4.H_2O$	Dark brown	9.34 (9.34)	10.29 (10.27)	35.31 (35.22)	3.92 (4.03)	16.81 (17.61)	1.78	17540 m (570)	$b_2—e_\pi^*$
								19840 m (504)	$b_2—b_1^*$
								22520 m (444)	$b_2—a_1^*$ + C—T
VO(H_2Salth)SO_4. CH_3OH	Dark violet	13.91 (14.02)	7.81 (7.71)	26.61 (26.44)	3.41 (3.30)	26.51 (26.44)	1.92	15870 m (630)	$b_2—e_\pi^*$
								23260 m (430)	$b_2—b_1^*$
								25380 m (395)	$b_2—a_1^*$ + C—T
VO(Salth)Py.$3CH_3OH$	Black	12.41 (12.48)	10.31 (10.29)	43.92 (44.12)	5.78 (5.68)	—	1.48	14080 mb (710)	$b_2—e_\pi^*$
								17540 mb (570)	$b_2—b_1^*$
								23800 m (420)	$b_2—a_1^*$ + C—T
VO(Salth) (pic). $3CH_3OH$	Black	11.92 (12.06)	9.90 (9.95)	45.51 (45.49)	6.01 (5.97)	—	1.54	15870 m (633)	$b_2—e_\pi^*$
								19150 m (522)	$b_2—b_1^*$
								20400 m (490)	
								21600 m (493)	$b_2—a_1^*$ + C—T
VO(Salth).$4CH_3OH$	Dark violet	14.18 (11.11)	7.74 (7.75)	36.07 (36.57)	5.91 (6.14)	–	1.34		

TABLE 2—IMPORTANT IR BANDS OF LIGANDS AND VANADYL COMPLEXES

Ligand/Complex	ν(NH)+ν(OH) +ν(C—H)	$\delta(NH_2)$	ν(NH)+ν(C=N) Thioamide band I	II	ν(V=O)	ν(C=S) Thioamide band IV	ν(M—N) +ν(M—S)	SO_4 bands ν_3	ν_4
pth	3220 sh	1598 s	1530 s	1375		840 s			
$VO(pth)_2SO_4$	3170 sb	1570 mb	1570	1345	970 s	820 w		1120 1070 w	
p-anth	3248 sb 3185 w	1603 vs	1530	1386 s		840 s			
$VO(p\text{-anth})_2SO_4.H_2O$	3410 sb 3200 sb	1600 vs	1570 m	1440 m	975 vs	830 w	435 w 340 sh	1178 s 1130	615 sp
H_2Salth	3275 sb 3235 mb	1605 s	1500 sb	1365		930 vs			
$VO(H_2Salth)SO_4$. CH_3OH	3240 sb	1605 sb	1555 w	1410 w	975 vs	905 m		1190 b 1150 1130 b	615
VO(Salth)Py. $3CH_3OH$	3430 svb 3240 mb	1595 s	1550 m	1395 w	975 vs	700 w	460 m 330 w		
VO(Salth)(pic). $3CH_3OH$	3430 svb 3240 mb	1590 s	1550 m		972 vs	705 w	465 m 430 w		
$VO(Salth).4CH_3OH$	3405 svb	1600 sb	1550 w		970 vs	705 w	462 w 340 w		

s = strong ; w = weak ; v = very ; sh = shoulder ; sp = sharp ; m = medium and b = broad.

neutral inner complexes, with H_2Salth, it disappears and a new weak band appears near 705 cm^{-1}. These facts support that the bonding of H_2Salth in neutral inner complexes takes place by deprotonation of thiol sulphur but in sulphato complexes, VO (H_2-Salth)SO_4. CH_3OH, thiohydrazide coordinate through thione sulphur.

The IR spectrum of sulphato complex VO(H_2-Salth) SO_4. CH_3OH displays splitting of ν_3 band of SO_4 group (Table 2) into three bands similar to bidentate sulphate groud[16, 17]. The ranges of splitted bands are similar to bridging sulphato group. The IR spectra of bischelated complexes, VOL_2SO_4. nH_2O (L = pth or *p*—anth and n = O or 1) display splitting of ν_3 vibration in two bands (Table-2) similar to monodentate sulphato group[17]. The Raman active ν_1 (SO_4) vibration has also been observed in these sulphato complexes as observed for coordinated sulphate group.

In far infrared region, the complexes display two to three medium to weak bands. These bands are tentatively assigned to M-N and M-S vibrations[18].

From stoichiometry, magnetic and spectral properties, it can be inferred that the structure of VOL_2 $SO_4.nH_2O$ (L = pth, fth or *p*-anth and n = 0 or 1) is straight forward while those of VO(H_2Salth)SO_4. CH_3OH and VO(Salth)B.$3CH_3OH$ (B = CH_3OH, pyridine or β-picoline) are complicated. The probable structures of the complexes are shown in Figs. A & B, respectively.

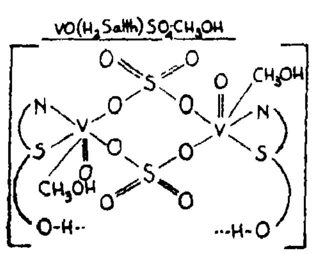


Fig A

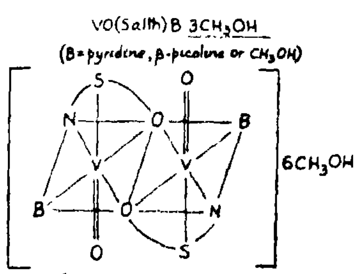


Fig B

References

1. (a) R. C. AGGARWAL, B. N. YADAV and T. PRASAD, *J. Inorg. Nuclear Chem.*, 1973, 35, 653 ; 1975 37, 899.
   (b) R. C. AGGARWAL and T. R. RAO, *Transition Met. Chem.*, 1977, 2, 21, 59, 201.
2. A. DUTTA AHMED and N. RAY CHAUDHURY, *J. Inorg. Nuclear Chem.*, 1971, 33, 189.
3. R. C. AGGARWAL and K. K. NARANG, *Indian J. Chem.*, 1976, 14A, 64 and references therein.
4. R. C AGGARWAL and T. R. RAO, *J. Inorg. Nuclear Chem.*, 1978, 40, 171.
5. J. GABEL, E. LARSEN and P. TRINDERUP, *Acta Chem. Scand.*, 1977, 31A, 657.
6. K. A. JENSEN and J. F. MIQUEL, *Acta Chem. Scand.*, 1952, 6, 189.
7. E. LARSEN, P. TRINDERUP, B. OLSEN and K. J. WATSON, *Acta Chem. Scand.*, 1970, 24, 261.
8. J. R. DILWONTH, J. H. P. VELLA, K. VENKATASUBRAMAMAN and JON. A. ZUBEETA, *Inorg. Chem.*, 1979, 18, 268.
9. R. W. BOST and O. L. SHEALY, *J. Amer. Chem. Soc.*, 1951, 73, 25.
10. S. P. GHOSH and L. K. MISHRA, *Inorg. Chim. Acta*, 1973, 7, 547.
11. R. H. HOLM, G. W. EVERETT JR. and A. CHAKRAVORTY, *Prog. Inorg. Chem.*, 1966, 7, 119.
12. C. C. LEE, A. SYAMAL and L. J. THERIOT, *Inorg. Chem.*, 1971, 10, 1669,
13. S. M. HORNER, S. Y. TYREE and D. L. VENEZKY, *Inorg. Chem.*, 1962, 1, 844.
14. C. J. BALLHAUSEN and H. B. GRAY, *Inorg. Chem.*, 1962, 1, 111.
15. J. SELBIN, H. R. MANNING and G. CESSAC, *J. Inorg. Nuclear Chem.*, 1963, 25, 2 53.
16. K. NAKAMOTO, "Infrared and Raman Spectra of Inorganic and Coordination Compounds" John Wiley, New York, Ed. 1977.
17. A. EARNSHAW, L. F. LARKWORTHY and K. C. PATEL, *J. Chem. Soc.*, (A), 1969, 1339.
18. D. M. ADAMS, "Metal Ligand and Related Vibrations", Edward Arnold Publishers, London, Ed. 1967, p. 325.

J. Indian Chem. Soc.,
Vol. LVII, March 1980, pp. 259-261

N-9-Anthracylidene-*p*-Dimethylaminoaniline Complexes of Some Transition Metals

P. SINGH*, V. SINGH, G. P. POKHARIYAL, R. PAL and R. P. MAHESH

Department of Chemistry, S. S. V. College, Hapur-245 101, (U. P.)

Manuscript received 30 July 1979, accepted 20 December 1979

N-9-Anthracylidene-*p*-dimethylaminoaniline has been used to isolate the complexes of Ti(IV), Zr(IV), Hf(IV), Th(IV), Ni(II) and Co(II). These were characterised by elemental analysis, magnetic, conductometric, electronic spectral and I.R. spectral studies. Magnetic and electronic spectral studies have been utilised to elucidate the tetragonal distortion from regular cubic symmetry of some of these complexes.

SCHIFF bases have been widely used as complexing agents.[1-3]. N-9-Anthracylidene-*p*-dimethylaminoaniline (abbreviated as ADAA) consists of acyl (C=O) and azomethine (CH=N—) groups in appropriate position and hence it may produce chelate compounds. It was therefore decided to isolate and characterise the chelate compounds of Ti(IV), Zr(IV), Hf(IV), Th(IV), Ni(II) and Co(II). The effect of distortion from regular cubic symmetry in some complexes produced due to nitrate and thiocyanate ligands of unequal donor strengths has also been discussed.

Experimental

The method of Kronke and Gross[4] was employed to prepare the Schiff base N-9-anthracylidene-*p*-dimethylaminoaniline by condensing 9-anthracene-glyoxal hydrate and *p*-dimethylaminoaniline in ethanolic medium, m.p. 78°C (Found : C, 81.24 ; H, 5.46 ; N. 7.84 ; requires : C, 81.80 ; H, 5.68 ; N, 7.93 ; percent).

All the metal salts $TiCl_4$, $ZrCl_4$, $HfCl_4$, $ThCl_4$, $Ni(NO_3)_2$, Ni $(NCS)_2$, $Co(NO_3)_2$ and $Co(NCS)_2$ used werie of A.R. quality and their metal contents were estmated by standard methods.

Carbon, hydrogen and nitrogen analyses were carried out at the Microanalytical laboratory, I.I.T. Kanpur. The conductance, magnetic and spectral studies were carried out by the reported methods[1-3]. Electronic spectra were studied both in solid state and in solution in acetone.

Isolation of Complexes :

Coloured solutions obtained on mixing equimolar solutions of the metal salts and the ligand in ethanol in stoichiometric 1 : 2 (metal : ligand) were refluxed for 2.5-5.5 hrs on steam bath. The reaction mixtures were cooled by refrigeration for few hours to few days and coloured crystals of the complexes were obtained which were washed with water, ethanol, ether and methylcyanide and dried in vacuum dessicator. Ethanolic solutions of Ti(IV), Zr(IV), Hf(IV) and Th(IV) complexes yielded white precipitate with ethanolic silvernitrate solution indicating thereby the presence of chlorine outside the co-ordination sphere of these complexes.

Molecular weights of the complexes were determined by cryoscopic method in bromoform medium. Magnetic moments were determined in powder form on Guoy's Balance and molar conductance measurements were carried out in NM medium. Analytical data colour and physical properties of the complexes are cited in Table 1.

Results and Discussions

Ti(IV), Zr(IV), Hf(IV), Th(IV), Ni(II) and Co(II) form 1 : 2 (metal : ligand) complexes. All these complexes are insoluble in water but soluble in the organic solvents such as DMSO, DMF, NM, bromoform and benzene. Ni(II) and Co(II) complexes show nonelectrolytic nature[6] whereas the other complexes exhibit biunivalent electrolytic nature[7-8]. Molecular weights were determined by cryoscopic method using bromoform as the solvent and these are in good agreement with the calculated values. The electronic spectral data in solid state and solution are identical showing thereby no change in structure of the complexes in the two states.

Magenetic Studies :

Ti(IV), Zr(IV), Hf(IV) and Th(IV) complexes exhibit magnetic moments 0.11-0.28 B.M. showing thereby octahedral symmetry[9] of the complexes. Nitrate and thiocyanate complexes of Ni(II) and Co(II) show magneticmoments 2.72,2.69 B.M. and 3,96,4.02 B.M. These values are slightly lower than the usual range 2.95-3.68 B.M. and 4.65-5.2 B.M. as reported

For correspondence : Dr. P. Singh, Mohalla-Ramnagar, Gulaothi. Bulandshahr, (U.P.).

TABLE—1. COLOUR AND ANALYTICAL DATA OF THE COMPLEXES

Compound	Colour	% Elemental analysis Calcd. (Found) C	Calcd. (Found) H	Calcd. (Found) N	Calcd (Found) Halogen	Calcd. (Found) Metal	Molar conductance λmohm^{-1} cm^{2} (in NM)	μ_{eff}(B.M.)	Molecular weight (in Bromoform) Calcd.	Found
$[Ti(C_{24}H_{20}N_2O)_2]Cl_2$	Violet	64.43 (64.00)	4.47 (4.23)	6.26 (6.10)	15.89 (15.02)	5 36 (5.18)	175	0.11	894	875
$[Zr(C_{24}H_{20}N_2O)_2Cl_2]Cl_2$	Blue	61.46 (61.08)	4.26 (4.19)	5.97 (5.78)	15.16 (15.00)	9.73 (9.68)	160	0.18	937	918
$[Hf(C_{24}H_{20}N_2O)_2Cl_2]Cl_2$	Pink	52.96 (52.78)	3.90 (3.75)	5.46 (5 37)	13.06 (12.82)	17.44 (17.16)	182	0.22	918	902
$[Th(C_{24}H_{20}N_2O)_2Cl_2]Cl_2$	Violet	52.90 (52.00)	3 68 (3.59)	5.15 (5.00)	13.04 (12.96)	21.04 (20.85)	158	0.28	1078	1056
$[Ni(C_{24}H_{20}N_2O)_2(NO_3)_2]$	Bluish Green	66.95 (66.52)	4.51 (4.40)	9.47 (9,28)	-	6.62 (6.59)	50	2.72	886.7	872
$[Ni(C_{24}H_{20}N_2O)_2(NCS)_2]$	Green	68.26 (68.00)	4.55 (4.42)	9.55 (9.36)	-	6.68 (6.59)	32	2.96	878.7	868
$[Co(C_{24}H_{20}N_2O)_2(NO_3)_2]$	Pink	66.94 66.49)	4.51 (4.42)	9.47 (9.51)	-	6.62 (6.56)	35	3.96	886.9	860
$[Co(C_{24}H_{20}N_2O)_2(NSC)_2]$	Violet	(68.24 (68.00)	4.55 (4.46)	9.55 (9.44)	-	6.68 (6.60)	28	4.02	878.9	870

for high spin octahedral complexes of Ni(II) and Co(II). It has been possible due to the lowering of O_h symmetry, thus suggesting distortion which is further confirmed by the electronic spectral studies.

Electronic Spectral Studies :

In the electronic spectra of $[Ni(C_{24}H_{20}N_2O)_2(NO_3)_2]$ and $[Ni(C_{24}H_{20}N_2O)_2(NCS)_2]$ four peaks have been observed at 9600, 12550, 17400, 29000 cm^{-1} and 8150, 12200, 15020, 26260 cm^{-1} in solution whereas spectra in solid state exhibit peaks at 9560, 12510, 17385, 29100 cm^{-1} and 8125, 12190, 15000, 26400 cm^{-1} showing a close agreement. First two bands in each case may be due to the splitting of ν_1 band because of the low symmetry of the ligand field or due to spin-forbidden transition whereas the last two bands characterise O_h symmetry. Careful scrutiny of the spectra in solution state, provides the following informations that it is not a spin-forbidden transition but a low symmetry component of the ν_1 band.

(i) Calculated ν_2 and ν_3 are 16146, 1341 cm^{-1} and 30248, 27000 cm^{-1} respectively which differ conside bly to the experimental values, showing thereby tetragonal distortion of O_h symmetry.

Corresponding experimental values of the bands are 17400, 15020 cm^{-1} and 29000, 26200 cm^{-1} respectively.

(ii) The ratios ν_2/ν_1 for these complexes are 1.82 and 1.82 which are greater than the usual range 1.5-1.76 as reported[10] for the O_h symmetry, indicating thereby tetragonal distortion of O_h symmetry.

(iii) However, the difference of $(\nu_3-\nu_2)$ calcd. and $(\nu_3-\nu_2)$ obs. for octahedral symmetry is small but here this difference appears to be 6302 cm^{-1} and 6789 cm^{-1}. This difference is comparable to tetragonally distorted octahedral complexes[11].

(iv) The values of B calculated for the present complexes are 1173 cm^{-1} and 1122 cm^{-1} which are greater than the free ion value 1080 cm^{-1}. It may be assumed due to tetragonal distortion[12] of octahedral symmetry.

On the basis of the above facts it is concluded that the bands at 12550 cm^{-1} and 12200 cm^{-1} as experimentally observed are the low symmetry components. Therefore, for tetragonally distorted octahedral complexes with nitrate and thiocyanate ligands co-ordinated along Z-axis, the most favourable transitions for the first two bands are $^3B_{1g} \longrightarrow {}^3B_g$ (9600 cm^{-1}, 8150 cm^{-1}) and $^3B_{1g} \longrightarrow {}^3B_{2g}$ (12550 cm^{-1}, 12200 cm^{-1}) having energies (10 D_q - $\frac{35}{4}$Dt) and 10 $D^2{}_q$ [8] in terms of radial parameters. The parameter Dt directly related to tetragonal distortion comes out to be 337 cm^{-1} and 463 cm^{-1}. The field along Z-axis is much weaker than along the xy plane as revealed by the parameters D_q (x,y), 1255 cm^{-1}, 1220 cm^{-1} and D_q (z), 295 cm^{-1}, 405 cm^{-1}, supporting thereby the reduced values of magnetic moments.

In the electronic spectra of Co (II) complexes in solution in acetone three bands at 8400, 8050 cm^{-1} [$^4T_{1g}$ (F) $\longrightarrow$ $^4T_{2g}$ (F) (ν_1)]; 18850, 18600 cm^{-1} [$^4T_{1g}$ (F) $\longrightarrow$ $^4A_{2g}$ (F) (ν_2)] and 24700, 24500 cm^{-1} [$^4T_{1g}$ (F) $\longrightarrow$ $^4T_{1g}$ (P) (ν_3)] have been observed whereas the calculated band positions (ν_2) are 19100 cm^{-1} and 18737 cm^{-1} respectively which are in close agreement with the experimental band positions. It may be taken as a measure of tetragonal distortion[12-14] of O_h symmetry. Spectral bands of these two complexes in solid state appeared at 8350, 8325 cm^{-1} ; 18760, 18500 cm^{-1} which are identical to those as observed in solution state.

Splitting energy parameter (10 D^q), racah parameter B and nephelauxetic ratio β of Co (II)

complexes are 9830, 9408 cm^{-1} ; 1024, 980 cm^{-1} and 0.91, 0.87 respectively. Nephelauxetic ratio β happening due to the partial overlaping of 3d orbitals with σ and π orbitals of the ligand consists of both $f^2\ \sigma$ and $f^2\ \pi$ i.e. $f^a = f^a\ \sigma.\ f^a\pi$ and are 0.91 and 0.87, showing thereby the coincidency to the values as have been observed for tetragonally distorted[15] octahedral complexes of Co (II).

Infrared Spectral Studies :

IR spectra of the complexes as compared to that of the ligand show lowering of stretching frequencies of active carbonyl (=C=O) and azomethine (—CH=N—) groups such as 1700 cm^{-1} to 1630-1650 cm^{-1} and 1600 cm^{-1} to 1520-1560 cm^{-1} respectively, indicating the formation of complexes through these groups. Appearance of bands at 425-465 cm^{-1} and 475-550 cm^{-1} indicate the formation of metal-oxygen (M-O) and metal-nitrogen (M-N) bonds, supporting thereby chelation through oxygen and nitrogen atoms. However, peaks around 325-425 cm^{-1} are observed in the IR spectra of complexes of Ti (IV), Zr(IV), Hf(IV) and Th(IV), thus revealing the formation of metal-halogen (M-Cl) bonds.

The nitrate complexes of Ni (II) and Co (II) exhibit bands at 1290 cm^{-1} and 1280 cm^{-1} in their IR spectra, showing thereby that the complexes are nitrate-bonded[16].

The thiocyanate complexes show stretching vibrations at 2080-2150 cm^{-1} and 690-810 cm^{-1} respectively, corresponding to C$\equiv$N and C-S. However, in spectra of the present complexes bands at 2040, 2045 cm^{-1} and 800, 825 cm^{-1} are observed, indicating the co-ordination of thiocyanate ion with the metal ions through N-atom[17].

Acknowledgement

Co-operation of Dr. R. C. Saxena is highly appreciated. Sincere thanks to U. G. C., New Delhi are gratefully acknowledged for providing financial assistance.

References

1. P. Singh, V. Singh, B. P. Singh and R. P. Mahesh, *Indian. J. Chem.*, 1275, 13, 734.
2. K. Dey and K. Sen, *J. Indian Chem. Soc.* 1975, 52, 261.
3. P. Singh, V. Singh, B. P. Singh, R. L. Goel and R. P. Mahesh, *Curr. Sci.*, 1976, 45, 137.
4. F. Kronke and K. F. Gross, *Chem. Ber.*, 1959, 92, 36.
5. M. P. Teotia, D. K. Rastogi and W. U. Malik, *Inorg. Chim. Acta*, 1973, 7, 340.
6. C. M. Harris and E. D. Mekenzie, *J. Inorg. Nuclear Chem.*, 1965, 4, 407.
7. N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 1959, 3997.
8. D. K. Rastogi and K. C. Sharma, *J. Inorg. Nuclear Chem.*, 1974, 36, 2220.
9. R. K. Upadhyay and V. P. Singh, *J. Indian. Chem. Soc.*, 1974, 51, 831.
10. D. K. Rastogi and K. C. Sharma, *J. Inorg. Nnclear Chem.*, 1974, 36, 2222.
11. O. Bostrup and C. R. Jorgensen, *Acta Chem. Scand.*, 1957, 11, 1223.
12. A. B. P. Lever, *Inorg. Chem.*, 1965, 4, 1042.
13. G. R. Burb, *Inorg. Chem.*, 1968, 7, 277.
14. B. Singh and U. Agrawal, *Inorg. Chem.*, 1969, 8, 2341.
15. D. K. Rastogi and K. C. Sharma, *J. Inorg. Nuclear Chem.*, 1974, 36, 2225.
16. B. M. Gatehouse, S. E. Livingstone and R. S. Nyholm, *J. Inorg. Nuclear Chem.*, 1958, 8, 75.
17. J. L. Burmeister, *Co-ord. Chem. Rev.*, 1968, 3, 225.

J. Indian Chem. Soc.,
Vol. LVII, March 1980 pp. 262-264

Mixed Ligand Thiocyanato Complexes of Cobalt(II)-Coordination Number Six and Eight

S. C. MAHAPATRA and D. V. RAMANA RAO*

Department of Chemistry, Regional Engineering College, Rourkela-769 008

Manuscript received 23 August 1979, accepted 30 December 1979

Dithiocyanato *bis*-(2-aminobenzothiazole) Cobalt(II) complex-$Co(ABT)_2(SCN)_2$ was reacted with a variety of nitrogen donor ligands in a mixed solvent medium. One hexa-coordinated compound-$Co(ABT)_2(SCN)_2Py_2$- and three octa-coordinated complexes of the type $[Co(ABT)_2(SCN)_2L_4]$ where L = β-picolline, γ-picoline and isoquinoline, were isolated and characterised by analysis, conductance, magnetic susceptibility, infrared and electronic spectroscopy and thermal decomposition.

THE chemistry of thiazole system has been extensively studied as the C^2 of the thiazole ring is the active site of vitamin B_1 (Thiamin Pyrophosphate)[1,2]. Also several metal complexes with substituted benzothiazoles[3] have been recently described. The substituents at 2,4 and 5 positions of the benzothiazole ring modify both the stoichiometry and the stereochemistry of the complexes[4,5]. It is known[6] that in thiocyanato complexes various factors like the effect of other ligands including their bascity and steric hindrance, π-bonding and preparative conditions control the mode of bonding of the ion to the metal. Cobalt(II) has a $3d^7$ non-bonding shell and usually forms tetrahedral or octahedral complexes utilising $4s4p^3$ or $4s4p^34d^2$ bonding orbitals. But the possibility of its exhibiting higher coordination numbers can not be ruled out under favourable ligand environment and experimental conditions. In this communication, Cobalt(II) complexes wherein the metal ion is surrounded by 2-aminobenzothiazole, thiocyanate, pyridine or substituted pyridine are studied and reported.

Experimental

Preparation of $[Co(ABT)_2(SCN)_2]$:

Dithiocyanato *bis*-(2-aminobenzothiazole) Cobalt (II) was prepared by the procedure described in the literature[5] and characterised by estimating the metal and the thiocyanate.

Preparation of $[Co(ABT)_2(SCN)_2L_2]$ *and* $[Co(ABT)_2(SCN)_2L_4]$:

To a hot ethanolic solution of dithiocyanato *bis*-(2-aminobenzothiazole) Cobalt(II), slightly more than the stoichiometric amounts of nitrogen donor ligands were added separately followed by the addition of Carbon tetrachloride (2/1 v). Immediately the colour changed from royal blue to pink. On refluxing the contents for nearly an hour and cooling, crystalline compounds seperated out. In case of isoquinoline complex, the volume was reduced and then kept over night to get the product. These were filtered, washed with ethanol, petroleum ether and dried over calcium chloride *in vacuo*.

Physical measurements :

The purity of the complexes was established by estimating the metal and thiocyanate by standard methods. The conductance measurements were carried out on M/1000 solutions in acetone using a Toshniwal Conductivity bridge type CL 0102 and a dip type cell. Magnetic susceptibility measurements were made over solid specimens using Gouy balance. Infrared absorptions were recorded on nujol and hexachlorobutadiene mulls using Unicam SP-200 double beam spectrophotometer. The electronic spectra in acetone were recorded using Unicam SP-500 and Carl Zeiss PMQ II Spectrophotometers. Thermogravimetric studies were carried out in a mannually operated thermobalance. Analytical and physical data for complexes are recorded in Table 1.

Results and Discussion

All the compounds are paramagnetic with μ_{eff} values ranging between 4.96 and 5.11 BM (Table-1). They are all spin free and the magnetic measurements indicate the presence of three unpaired electrons, the higher values being due to orbital contribution. For 1 : 1 electrolytes, the Δ_M values in acetone medium will be as high as 150 mhos[7] and the low values obtained now indicate that they are essentially non-electrolytes but undergo appreciable dissociation in solution.

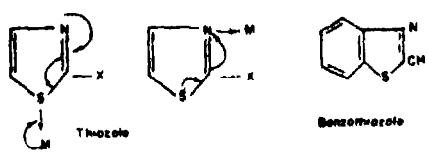
Infrared Spectra :

Thiazole is formally derived from imidazole by replacement of NH by S in 1-position which makes

TABLE 1—ANALYTICAL AND PHYSICAL DATA FOR MIXED LIGAND COBALT(II) COMPLEXES

Sl No.	Compounds	Colour & form	M. P. (°C)	% Cobalt Found	% Cobalt Calc.	% Thiocyanate Found	% Thiocyanate Calc.	ΛM (mhos)	μ_{eff} (B.M.)
1.	$[Co(ABT)_2(SCN)_2(\gamma\text{-pic})_4]$	Pink crystalline	175	6.90	6.93	13.62	13.65	31	3.09
2.	$[Co(ABT)_2(SCN)_2(\beta\text{-pic})_4]$	-do-	143	6.92	6.93	13.58	13.65	54	4.96
3.	$[Co(ABT)_2(SCN)_2(IQ)_4]$	Red crystalline	162	5.89	5.95	11.63	11.70	67	5.05
4.	$[Co(ABT)_2(SCN)_2(Py)_2]$	Pink crystalline	208	9.25	9.30	18.26	18.31	52	5.11

thiazole a better π-acceptor due to the availability of empty d orbitals on sulphur atom. For the structure outlined for thiazole and benzothiazole, it is expected that on coordination through either sulphur or nitrogen, C-S stretching vibration will increase, while C=N stretching frequency will remain almost unaltered or may increase slightly for metal-sulphur bonding and will decrease for metal-nitrogen bonding. Infrared spectra of the complexes



show the presence of strong absorption bands of both 2-aminobenzothiazole and nitrogen donor ligands, indicating definitely that they are mixed ligand complexes. As expected, the ligand absorption bands are modified as a result of bonding to the metal. Some bands are however masked in the absorption range of Nujol used as mulling agent. As pointed above benzothiazoles could coordinate to metal either through nitrogen or sulphur. In case of S-bonded benzothiazole, significant changes in the range of 600-1600 cm^{-1} are shift of bands at 1475 cm^{-1} due to ν(C-N) and at 667 cm^{-1} due to ν(C-S) in the spectra of the free ligand. The C-S stretching frequency is shifted to a higher value on account of an increased $d\pi$-$d\pi$ contribution between sulphur and the ring π-system[8]. In the present case, the bands at ~ 700-725 cm^{-1} in the ν(C-S) region and at ~ 3270 cm^{-1} in the ν(N-H) region are indicative of the presence of 2-aminobenzothiazole bonded through sulphur atom with non-involvement of amino group in the complex formation[9]. Further the C=N stretching vibration of 2-aminobenzothiazole at ~ 1500 cm^{-1} got split and shifted to a higher frequency regions 1515-1565 cm^{-1} indicating that it is not N-bonded since in case of N-bonding, the ν(C=N) would have been decreased. The appearance of bands at ~ 1620 cm^{-1} region is due to the ν(C=N) of the heterocyclic base. The thiocyanate ion SCN^- is an ambidentate ligand and various modes of its coordination have been recently reviewed[10,11]. In the present compounds ν(C—N) bands appear in the region 2040-2084 cm^{-1} and ν(C-S) are observed in the region 690-760 cm^{-1} indicating the presence of S-bonded thiocyanate group.

Electronic Spectra :

The compounds undergo dissociation in solution which is evidenced by the pink solids giving blue solutions. Extra addition of the ligand to the compounds in solution does not seem to prevent this dissociation. The spectrum obtained is similar to that of a four coordinated species. In fact, the broad bands at ~ 16400 cm^{-1} region with high extinction coefficients (ϵ value ranging between 1020-1330) can be assigned to $4_{A2} \rightarrow 4_{T1}(P)$ transition corresponding to ν_3 of a species having tetrahedral symmetry[12]. Hence it is evident that in the solution stage, the complex has changed over to a tetrahedral form by dissociation. Attempts were made to prevent this dissociation in a solvent by recording the absorption using nujol mull filter paper technique. Here no absorption in the region corresponding to a tetrahedral or an octahedral symmetry was seen but no definite conclusion could be drawn regarding the coordination number. However, additional evidence was obtained from the thermogravimetric studies of the compounds.

Thermal Decomposition :

Thermal decomposition of pyridine complexes of Cobalt(II) halides was studied earlier[13] where pyridine was found to be lost gradually. The thermal behaviour of the compounds under report can be schematically represented as follows :

$[Co(ABT)_2(SCN)_2(\gamma\text{-pic})_4] \xrightarrow{110°} [Co(ABT)_2(SCN)_2(\gamma\text{-pic})_2] \xrightarrow{180°} Co(ABT)_2(SCN)_2$

Pink → Bluish pink → Blue

$[Co(ABT)_2(SCN)_2(\beta\text{-pic})_4] \xrightarrow{100°} [Co(ABT)_2(SCN)_2(\beta\text{-pic})_2] \xrightarrow{180°} Co(ABT)_2(SCN)_2$

Pink → Bluish Pink → Blue

$[Co(ABT)_2(SCN)_2(IQ)_4] \xrightarrow{125°}$

Red

$$[Co(ABT)_2(SCN)_2(IQ)_2] \xrightarrow{\text{[illegible]}^{\circ}} Co(ABT)_2(SCN)_2$$

Dull red — Blue

$$[Co(ABT)_2(SCN)_2(Py)_2] \xrightarrow{\text{[illegible]}^{\circ}} Co(ABT)_2(SCN)_2$$

Pink — Blue

Thus the thermal decomposition studies of octa-coordinated compounds reveal a stepwise loss of the heterocyclic bases leading to the formation of hexa-coordinated compounds which decompose further yielding the four-coordinated starting compound, $Co(ABT)_2(SCN)_2$. The weight losses and the analyses of the compounds after decomposition agree with the above formulation. Hence it is evident that the original compounds are octa-coordinated from which two moles of the nitrogen donor ligand are lost in the first stage to give hexa-coordinated compounds. However, x-ray studies alone can reveal the exact coordination number and the proposed stereochemistry of the complexes.

Acknowledgement

One of the authors (S.C.M.) is thankful to U. G. C., New Delhi for award of a teacher fellowship and to the Government of Orissa for granting study leave.

References

1. S.F. DYKE, "The Chemistry of Vitamins", (*Interscience*), New York, 1965, p. 4.
2. R. BRESLOW, "CIBA Study Group N", Little Brown and Co., Boston, p. 65.
3. N. N. Y. CHAN, M. GOODGAME and M. J. WEEKS, *J. Chem. Soc.* (A), 1968, 2499.
4. M. J. M. CAMPBELL, D. W. CARD, R. GRZESKOWIAK and M. GOLDSTEIN, *J. Chem. Soc.* (A), 1970, 672.
5. E. J. DUFF, M. N. HUGHES and K. J. RUTT, *J. Chem. Soc.* (A), 1969, 2101.
6. B. W. BROWN and E. C. LINGAFELTER, *Acta Crystallogr.*, 1963, 16, 753.
7. R. A. ROBINSON and R. N. STOKES, "*Electrolytic Solution*", Butterworth Publ. (Lond), 1959, Ed.
8. D. P. CRAIG, A. MACCOLL, R. S. NYHOLM, L. E. ORGEL and L. E. SUTTON, *J. Chem. Soc.*, 1954, 332.
9. R. N. DASH and D. V. RAMANA RAO, *J. Indian Chem. Soc.*, 1974, 51, 787.
10. J. L. BURMEISTER, *Coord. Chem. Rev.*, 1966, 1, 205 and 1968, 3, 225.
11. A. H. NORBURY and A. I. P. SINHA, "Quart. Rev.", 1970, 24, 69.
12. F. A. COTTON and G. WILKINSON, "Advanced Inorganic Chemistry", (2nd Ed.), Wiley Eastern Private Ltd., 1969, p. 871.
13. D. H. BROWN, D. KENYON and D. W. A. SHARP, *J. Chem. Soc.*(A), 1969, 1474.

J. Indian Chem. Soc.,
Vol. LVII, March 1980, pp. 265-267

Determination of Stability Constants of 2-Hydroxy-1-Naphthalidene-2'-Methyl-4'-Nitraniline Complexes with Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}

M. S. MAYADEO and S. S. PUROHIT

Department of Chemistry, Ramnarain Ruia College, Bombay-400 019

Manuscript received 6 February 1979, revised 24 September 1979, accepted 19 November 1979

Potentiometric studies have been carried out on metal complexes of Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} with 2-hydroxy-1-naphthalidene-2'-methyl-4'-nitraniline. The dissociation constants (pK_1 & pK_2) of the reagent and the formation constants of its metal complexes have been determined by Bjerrum's method at 25°±0.1° and at an ionic strength 0.1*M* in 75 : 25 percent (v/v) dioxan-water medium.

IN *the present communication the* successive stability constants of the complexes of 2-hydroxy-1-naphthalidene-2'-methyl-4'-nitraniline with various bivalent metal ions have been determined potentiometrically following the Calvin-Bjerrum *p*H titration as adopted by Irving and Rossotti[1].

The Corning Model 12, a precision research *p*H meter with combined, glass electrode and a calomel reference electrode was used for *p*H measurements. Both electrodes dip into the titrating mixture, without vitiating any results. The meter has an arrangement for normal and expanded scale. The changes in the *p*H can be measured with an accuracy of 0.005 *p*H unit.

Experimental

The ligand 2-hydroxy-1-naphthalidene-2'-methyl-4'-nitraniline was prepared by dissolving 10 gm of 2-hydroxy-1-naphthaldehyde (Fluka) in 50 ml of absolute ethanol and to this was added equimolar quantity of *o*-methyl-*p*-nitraniline. This reaction mixture was refluxed on a water bath for half an hour. After cooling, the solution was filtered to get the crude product, which was repeatedly crystallised from alcohol to get analytically pure compound. The M. P. observed was 191°. Analytical results Found : C, 70.6 ; H, 5.00 ; N, 9.14 per cent. Calcd. for $C_{18}H_{14}N_2O_3$: C, 70.6 ; H, 4.60 ; N, 9.15 per cent.

The dioxan used for experimental work was purified by the method described by Vogel[2]. Distilled water redistilled over alkaline potassium permanganate was used throughout the investigation.

The medium of titration was 75 : 25 per cent dioxan-water (v/v) mixture. Sodium perchlorate was added to maintain a constant ionic strength. The *titrations were carried out in an inert atmosphere* by bubbling oxygen free nitrogen gas through the solutions. The free acid, the free acid plus the ligand and the mixture of metal ion containing the acid plus the ligand were titrated against standard carbonate free sodium hydroxide. Metal ion solutions of Nickel and Cobalt were prepared by taking the metal carbonates of A. R. grade, and those of copper and zinc were prepared by taking the metal oxides of A.R. grade. These were then converted to the corresponding metal perchlorates. All these were standardised complexometrically[3] by EDTA titrations. All the measurements were carried out at 25°±0.1°.

The following solutions were titrated potentiometrically against standard carbonate free sodium hydroxide (1.07*M*) solution.

(i) 5 ml. of (0.16*M*) $HClO_4$+5ml. of (0.64*M*) $NaClO_4$+30 ml. of dioxan.

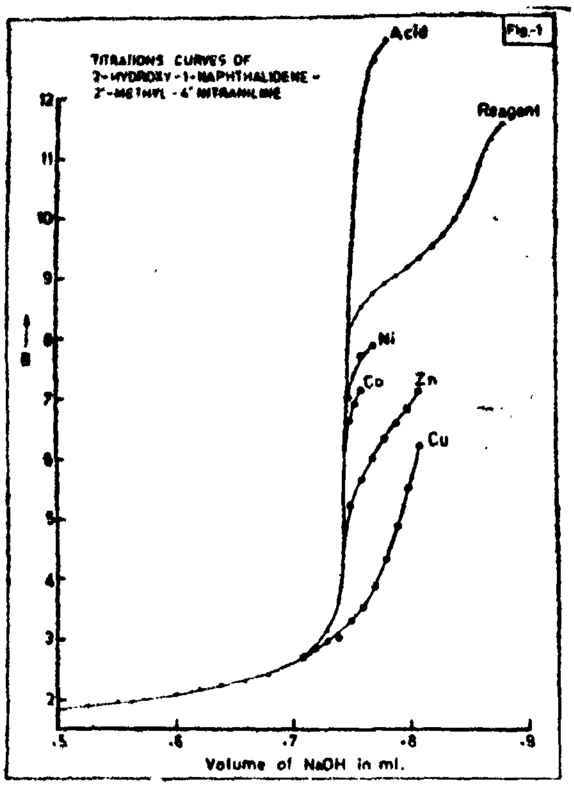
(ii) 5 ml. of (0.16*M*) $HClO_4^-$+5 ml. of (0.64*M*) $NaClO_4$+requisite amount of reagent accurately weighed to give 0.004*M* reagent concentration in the final solution+30 ml. of dioxan.

(iii) 5 ml. of (0.64*M*) $NaClO_4$+5 ml. of metal salt (0.008*M*) solution in (0.16*M*) $HClO_4$+the requisite amount of the reagent accurately weighed to give 0.004*M* reagent concentration in the final solution+30 ml. of dioxan.

The experimental method of Irving and Rossotti was applied to find out the values of $\bar{n}$ and pL. The titrations were performed in duplicate to test for the reproducibility.

Results and Discussion

It may be pointed out here that the ligand used in this study did not undergo hydrolysis under the experimental conditions described. This was indicated by rapid attainment of equilibrium during the titration and by the absence of any significant drift in the *p*H even after one hour.



In the ligand it is the chelated phenolic (OH) group which takes part in the complex formation and the proton is replaced from it by metal ions during chelation. Since only one proton per ligand molecule is liberated during complexation, 'Y', the number of dissociable protons attached to each ligand molecule is one.

From the titration curves (Fig. 1) using solutions (i) and (ii), $\bar{n}_A$ values at various 'B' values (*p*H meter readings) were calculated and a curve between 'B' and the corresponding $\bar{n}_A$ values was plotted. The formation curve extends over a range $0.39 \angle \bar{n}_A \angle 0.69$ and the value of pK^H was evaluated from the half integral point at $\bar{n}_A = 0.5$. The plot of log $\left[\frac{\bar{n}_A}{1-\bar{n}_A}\right]$ vs 'B' was also drawn. From this pK_1 was evaluated. This value agrees quite well with that obtained by half integral method.

From the titration curves of solutions (ii) and (iii) $\bar{n}$ and pL values were calculated. The $\bar{n}$ values were plotted against the corresponding pL values to get the formation curves of the metal complexion equilibria (Fig. 2). From these formation curves, the values of stability constants log K_1 and log K_2 were calculated which correspond to pL value at $\bar{n} = 0.5$ and $\bar{n} = 1.5$ respectively. The plots of log $\left[\frac{\bar{n}}{1-\bar{n}}\right]$ against pL and log $\left[\frac{2-\bar{n})}{(\bar{n}-1)}\right]$ against pL were also drawn. From the former log K_1 was evaluated and from the later log K_2, was evaluated. The values of log K_1 and K_2 agree quite well with those obtained by the half integral method.

The most representative values are recorded in

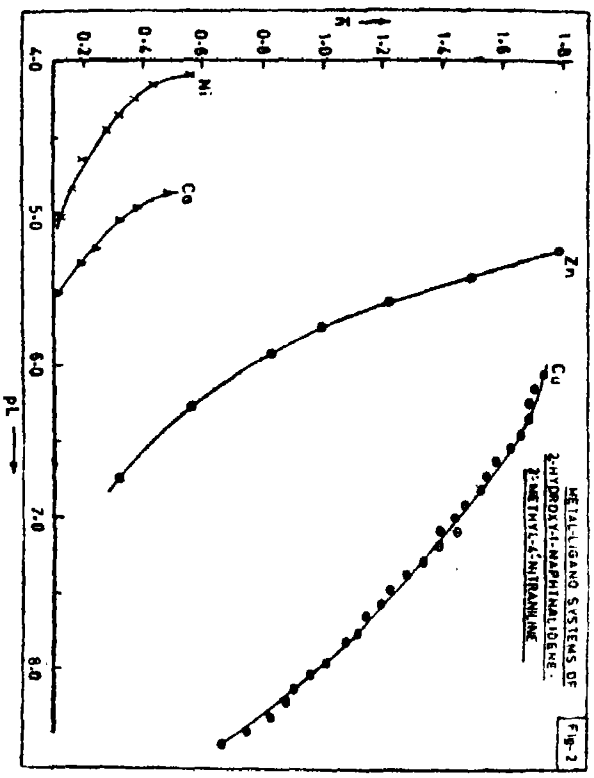


Table 1. The order of stability of the bivalent metal chelates was found to be $Cu^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+}$.

TABLE 1—STEPWISE STABILITY CONSTANTS OF VARIOUS COMPLEXES*

t = 25°C $\mu = 0.1$

Cations	Ni^{2+}	Co^{2+}	Zn^{2+}	Cu^{2+}	H^{1+}
log K_1	4.11	4.87	6.40	8.66	9.61
log K_2	-	-	5.40	6.91	-

* For proton association (H^+), K_1 corresponds to the species LH, while for metal ions K_1 and K_2 correspond to the species ML_1 and ML_2 respectively.

Acknowledgement

The authors wish to record their sincere thanks to Dr. D. G. Vartak, B.A.R.C., Bombay for his valuable suggestions and to Dr. R. A. Kulkarni Principal, Ramnarain Ruia College, Bombay for his kind and continuous encouragement in accomplishing this work.

References

1. H. M. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.*, 1954, 2904.
2. A. I. VOGEL, A. Text Book of Practical Organic Chemistry, III Edition, Longmans, p. 177.
3. H. A. FLASCHKA, 'EDTA Titrations', Pergamon Press, N. Y., p. 78.

J. Indian Chem. Soc.,
Vol. LVII, March 1980, pp. 268-269

Chelate Formation of Penicillins with Certain Tervalent Carcinogenic Metal Ions

P. B. CHAKRAWARTI*, (Km.) ANURADHA TIWARI and H. N. SHARMA

Chemistry Department, M. L. B. College, Bhopal

Manuscript received 10 October 1979, accepted 30 December 1979

Chelate formation of the two most common and widely used penicillins (penicillin-G and penicillin-V) has been studied with some tervalent carcinogenic metal ions e.g. Fe(III), Al(III) and Cr(III) using Calvin-Bjerrum's *p*H-titration technique as adopted by Irving and Rossotti in 50% aqueous-acetone solution at 30° and in 0.1*M* ionic strength ($NaClO_4$). The stepwise formation constants indicate the order of stability to vary as : Al(III) < Fe(III) < Cr(III). The maximum value of $\bar{n}$ reaches ~2 in every case, indicating formation of ML and ML_2 complexes only. This suggests that two coordination positions remain unoccupied with the expected octahedral geometry of the complexes, which may be utilised for combination with tissues.

CANCER formation and its inhibition both involve chelation. Carcinogenic metals are generally transition metals, which have pronounced tendency for chelation and are associated with vitamins, proteins and nucleic acids. In our earlier communications we reported chelate formation of these penicillins with certain bivalent metal ions[1-3], in the present communication we report the chelate formation of penicillin-G(PG) and penicillin-V(PV) with some carcinogenic tervalent metal ions e.g. Fe(III), Cr(III) and Al(III) in 50% aqueous acetone solution at 30° and 0.1 *M* ionic strength with $NaClO_4$, using Calvin-Bjerrum's *p*H-titration technique[4] as adopted by Irving and Rossotti[5].

Experimental

All the reagents employed were of high purity. The preparation and standardisation of the metal and the ligand solutions and the other experimental details remaining the same as given in the earlier communication[1].

Stoichiometry of the complexes formed was ascertained by potentiometric and conductometric titrations, utilising the monovariation method[6]. For conductometric studies WTW, LBR, Germany, conductivity-bridge, with the dip-type conductivity cell was used. 10 ml. of the ligand solution (0.01 *M*) was diluted to 100 ml. and was titrated with 0.01 *M* metal solution. The conductance were recorded after each addition of 0.5 ml. of the metal solution and were corrected to the dilution effect. *p*H-measurements were done on 'Systronics', *p*H-meter No. 322 using glass-calomel electrode assembly in conjunction with saturated calomel electrode.

The Bjerrum-Calvin[4] *p*H-titration technique as adopted by Irving and Rossotti[5] was followed to determine various formation constants. For *p*H titrations, the following mixtures keeping acetone-water ratio 1 : 1 in 50 ml. of the reaction solutions were titrated against carbonate free 0.2 *M* KOH :

(A) 5ml. of 0.04 *M* $HClO_4$
(B) Mixture (A)+10 ml. of 0.02 *M* Ligand.
(C) Mixture (B)+5 ml. of 0.002 *M* metal solution.

The ionic strength of the above solutions was maintained to 0.1 *M* by adding the required quantity of 0.1 *M* $NaClO_4$ solution. Correction for *p*H-measurements in 50% acetone-water system was done as described by Van-Uitert and Hass[7] and Irving-Rossotti[5]. On progressive addition of the alkali during the *p*H-titrations a precipitate was obtained in each case. The *p*H of precepitation in the different systems being : Fe-PG/PV, 5.6 ; Cr-PG/PV, 5.5 ; Al-PG ; 5.2 and Al-PV, 3.8. Therefore, in these cases all the calculations have been done below the *p*H of precepitations. Further, with the use of very dilute solutions ($1\times10^{-4}M$) of the metals, possibility of the formation of polynuclear complexes may be ruled out.

Metal-Ligand formation constants :

In the stepwise complex formation, the nth metal-ligand stability constant (K_n) is given by—

$$K_n=\frac{CML_n}{CML_{n-1}.CL} \cdots\cdots\cdots\cdots(n=1,2,\ldots\ldots n)$$

For plotting formation-curves (graph between average number of ligand bound to metal ($\bar{n}$) and free ligand exponent (pL), $\bar{n}$ and pL values were calculated using the equations :

$$\bar{n}=\frac{(V'''-V'')\,(N^o+E^o)}{(V^o+V'').\,\bar{n}_A\,.TCM^o}$$

*To whom correspondence should be addressed : 90/24, T-Nagar, Bhopal-462 005.

$$pL = \log_{10}\left[\frac{\sum_{n=0}^{n=J} \beta_n^H \left(\frac{1}{\text{antilog } B}\right)^n}{TCL^\circ - \bar{n}.\, TCM^\circ} \cdot \frac{V^\circ + V'''}{V^\circ}\right]$$

where TCM° is total concentration of metals ; B is the pH, β_n^H, overall proton ligand constant and V′, V″, V‴ are the volume of alkali required to reach the same pH in acid, ligand and metal titration curves, while N° and E° are the normality of alkali and strength of acid in 50 ml. of the solution. The values of log K_1, log K_2 and log β_2 were recorded directly from the formation curves and refined by the best least-square fits. The refined values are given in Table 1.

TABLE 1—STABILITY CONSTANTS : PENICILLIN COMPLEXES

$\mu = 0.1M$ ($NaClO_4$) Temp. : 30°C.

Metal	log K_1 PG	log K_1 PV	log K_2 PG	log K_2 PV	log β_2 PG	log β_2 PV
Al(III)	5.40	4.59	4.70	4.04	10.10	8.63
Fe(III)	5.47	4.80	4.75	4.06	10.23	8.86
Cr(III)	5.50	4.95	4.77	4.48	10.27	9.43

Results and Discussion

The conductometric and pH-titrations and the maximum values of $\bar{n}$ ($\sim$2) indicate formation of ML and ML_2 complexes in the systems studied.

The tervalent ions studied here include two transitional Cr(III) and Fe(III) and one nontransitional metal Al(III). According to the expectations and transitional metals complexes were found more stable. However, the order obtained for the complexes studied in this investigation does not follow the order suggested earlier by Irving-Williams[8] and Fernalies *et al*[9]. According to which Fe(III) complexes should have greater stability over that of Cr(III) ; but the order obtained here varies as ; Cr (III) > Fe(III) and follows the order of the second ionisation potential and e^2/r-ratio for the metallic ions. Thus, the order of stability obtained seems to follow the order of increasing polarisability :

$$P = \frac{Z-S}{r} \text{ where, } P = \text{Proportionality constant}$$

Z = atomic number, S = screening effect constant and r = radii. For the regular octahedral complexes, according to CFT the degenerated d-AO of the metal ion split into two new levels the lower triplet, t_{2g} electrons increases the screening effect in the direction perpendicular to the centres of the faces of the octahedron, hence do not influence the interaction between metal and ligand appreciably. While the number of electrons in eg AOs affect the screening effect linerly, thus, greater is the number of eg-electrons, weaker is the polarising effect and hence the metal to ligand bond. Fe(III) (ad^5) in an octahedral field, will have three electrons in t_{2g} and two electrons in eg-AOs, while Cr(III) $3d^3$) there will be no electron in eg AOs, resulting in the higher stability of its complexes due to polarising action.

Further, the stoichiometry of the complexes indicate formation of only two, ML and ML_2 complexes. This suggests that two coordination positions remain unoccupied with the expected octahedral geometry of the complexes, which may be utilised for combination with tissues.

References

1. A. TIWARI and P. B. CHAKRAWARTI, *J. Indian Chem. Soc.* 1980, **57**, 134.
2. A. TIWARI and P. B. CHAKRAWARTI, *Indian J. Chem.* 1980, **19A**, 83.
3. A. TIWARI and P. B. CHAKRAWARTI, *Proc. Nat. Acad. Sci.*, (In the process of publication).
4. A. E. MARTELL and M. CALVIN, "*Chemistry of the metal chelate compounds*", Printice Hall, N. Y. 1953, p. 192.
5. I. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.*, 1953, 3397.
6. M. R. NAIR and C. S. PANDE, *Proc. Ind. Acad. Sci.*, 1948, **27A**, 284.
7. L. G. VAN UITERT and C. HASS, *J. Amer. Chem. Soc.*, 1953, **75**, 3651.
8. H. IRVING and R. J. P. WILLIAMS, *Analyst*, 1952, **77**, 813.
9. W. C. FERNELIUS, R. M. IZATT, C. S. HASS and B. P. BLOCK, *J. Phys. Chem.*, 1955, **59**, 170.

J. Indian Chem. Soc.,
Vol. LVII, March 1980, pp. 270-272

Complexes of Zinc(II), Cadmium(II), Lead(II), Copper(I), Silver(I) and Thallium(I) with 4-Amion-5-Mercapto-3-Trifluoromethyl-1,2,4,-Triazole

R. V. GADAG and M. R. GAJENDRAGAD*

Department of Chemistry, Karnataka Regional Engineering College, Surathkal, P. O. Srinivasnagar-574 157, Karnataka

Manuscript received 10 October 1979, accepted 30 December 1979

Complexes of Zinc(II), Cadmium(II), Lead(II), Copper(I), Silver(I) and Thallium(I) with 4-Amino-5-mercapto-3-trifluoromethyl-1, 2, 4-triazole have been synthesised. The complexes are characterized based on analytical data, IR spectral studies, oxidation state study and magnetic susceptibility measurement. Tetrahedral structures are proposed for the complexes.

IN recent times, considerable interest is evinced in the study of complexing behaviour of mercapto derivatives of substituted 1,2,4-triazoles[1-3]. In continuation of our previous work on metal complexes[4,5] with substituted 1,2,4-triazoles, we report here the syntheses and characterisation of Zinc(II), Cadmium(II), Lead(II), copper(I), Silver(I) and Thallium(I) complexes with 4-Amino-5-mercapto-3-trifluoromethyl-1,2,4-triazole (Fig. 1).

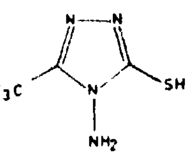


Fig. 1. The ligand-4-amino-5-mercapto-3-trifluoromethyl-1,2,4-triazole.

Experimental

All chemicals used were of AR or CP grade.

Preparation of the ligand : 4-Amino-5-mercapto-3-trifluoromethyl-1,2,4-triazole was prepared by the reported method[6].

General method of preparation of complexes : A warm alcoholic solution of the ligand in slight excess over the molar ratio, was added to aqueous solutions of lead acetate or nitrates/sulphates of other metal ions. Ammoniacal medium was used in the case of Cd(II) and Zn(II) solutions. White crystalline complexes of Zn(II), Cd(II), Pb(II) and Tl(I) were formed readily. They were filtered after cooling, washed thoroughly with 50% alcohol, sparingly with ethanol and finally with ether. They were dried over anhydrous $CaCl_2$ in a vacuum desiccator. All these complexes are fairly soluble in ethanol although they are almost insoluble in 50% alcohol. Complexes of Cu(I) and Ag(I) though white are not crystalline, but were formed readily. They were digested on water bath for 30 min. separated, purified and dried as described above.

Analyses :

Sulphur was estimated as $BaSO_4$ by alkali fusion method[4]. Metals were estimated by standard methods after destroying the ligand with Con.HNO_3 and heating to fuming with Con.H_2SO_4. Since micro analyses of C and H of fluorine containing complexes were not undertaken by any of the micro analytical sections in India, only the nitrogen analyses carried out on micro scale at CDRI, Lucknow, were used for determining the stoichiometry of the complexes.

Results and Discussion

Analytical data (Table 1) show that Zn(II), Cd(II) and Pb(II) form 1 : 2 (metal : ligand) complexes while Cu(I), Ag(I) and Tl(I) fom 1 : 1 (metal : ligand) complexes. The ligand readily reduces Cu(II) to Cu(I) and forms a stable Cu(I) complex. The +1 oxidation state of copper in its complex was confirmed by redox studies[7]. Further evidence in support of this comes from diamagnetic behaviour of Cu(I) complex.

Infrared Spectra :

Since the ligand molecule contains a thioamide moiety (H-N-C = S), it can exist in thiol as well as thione forms. A weak band at 2490 cm^{-1} in the IR

*For correspondence.

spectrum of the ligand suggests the presence of -SH group while a strong band at 790 cm^{-1} indicates the presence of C=S group. Since most of the metal ions under study belong to 'b' class or lie on borderline and some of them are highly polarizable, complex formation is greatly favoured at readily polarizable donor site viz. S where back bonding can occur. The IR spectral data lend support to this view.

The conspicuous absence of the ν(S-H) band in the spectra of all complexes is an indication of bonding through thiol sulphur after deprotonation. Further evidence in support of this comes from systematic shifts in the thioamide band positions[8] in the IR spectra of the complexes as compared with those for the ligand (Table 2). Thioamide band II [ν(C=N) + δ(N−H)] appearing around 1250 cm^{-1} experiences a blue shift of about 30 cm^{-1} in the spectra of the complexes. This is a consequence of metal ion bonding through sulphur which would doubtless localize the double bond between C and N and shift the position of band II towards higher wave number side.

Thioamide band IV (Due mainly to ν(C=S)) obseved at 790 cm^{-1} in the spectrum of the ligand registers considerable red shift of about 40 cm^{-1} in the spectra of the complexes. This lends additional support to sulphur atom being the site of coordination. In addition, the positions of thioamide bands I and III are considerably shifted towards lower wave number side. The IR bands in the region of 3100-3300 cm^{-1} due to ν(N-H) of the primary amino group is slightly shifted towards lower number side. This indicates the participation of the N atom of the amino group in chelation with metal ions. Besides these observations, new bands around 400 cm^{-1} due to ν(M-N) and around 350 cm^{-1} due to ν(M-S) are also observed in the IR spectra of the complexes. These results are in Confirmity with the proposed mode of likage. Based on the stoichiometry, IR data of the complexes and preferences of these metal ions for the tetrahedral geometry, tetrahedral structures are proposed for the complexes. However, two coordinate linear polymeric structures for Cu(I), Ag(I) and Tl(I) cannot be ruled out altogether although no definite evidence could be had to decide it conclusively.

TABLE 1—ANALYTICAL DATA OF LIGAND AND METAL COMPLEXES

Compound	Found % N	Found % S	Found % Metal	Calc. % N	Calc. % S	Calc. % Metal
$C_8H_8F_3N_4S$	30.13	17.47	-	30.43	17.48	-
$Zn(C_8H_7F_3N_4S)_2$	26.12	14.85	14.93	25.96	15.14	14.85
$Cd(C_8H_7F_3N_4S)_2$	23.29	13.12	23.24	23.41	13.40	23.48
$Pb(C_8H_7F_3N_4S)_2$	19.41	(11.46)*	35.98	19.54	11.18	36.13
$Cu(C_8H_2F_3N_4S)$	22.58	13.15	25.74	22.71	13.00	25.76
$Ag(C_8H_7F_3N_4S)$	19.31	11.20	37.05	19.25	11.02	37.07
$Tl(C_8H_2F_3N_4S)$	14.55	7.97	52.53	14.46	8.27	52.74

*Found by difference.

TABLE 2—THIOAMIDE BANDS (IN CM^{-1}) IN THE LIGAND AND METAL COMPLEXES

Compounds	Band-I δN-H + νC=N	Band-II νC=N + δN-H	Band-III νC-N + νC=S	Band-IV νC=S
LH	1580 S	1250 Ss	1090 Ss	790 ms
ZnL_2	1550 m	1275 Ss	1060 S	735 wb
CdL_2	1540 w	1285 ms	1065 ms	740 wb
PbL_2	1540 m	1275 S	1040 w	735 wb
CuL	1545 Ss	1275 Ss	1045 S	735 mb
AgL	1535 wb	1275 w	1055 w	735 wb
TlL	1540 mb	1265 ms	1040 mb	750 wb
Shift	red (35±5)	blue (25±10)	red (40±10)	red (40±15)

LH = $C_8H_8F_3N_4S$
S = strong, s = sharp, m = medium, w = weak and b = broad.

Acknowledgement

The authors are thankful to Prof. K. Mahadevan, Principal and Prof. T. J. Varkey, Head of the Chemistry Department, Karnataka Regional Engineering College, for providing financial assistance, laboratory facilities and all round help.

References

1. B. K. SINHA, RAJESHWAR SINGH, J. P. SRIVASTAVA and L. K. MISHRA , *J. Inorg. Nuclear Chem*. (U. K.), 1977, 39, 1797.
2. BIRENDRA KUMAR GUPTA, D. S. GUPTA, S. K. DIKSHIT and U. AGARWALA, *Indian J. Chem*., 1977, 15A, 624.
3. BIRENDRA KUMAR GUPTA, D. S. GUPTA and U. AGARWALA, *Bull. Chem. Soc*. (Jap.), 1978 51, 2724.
4. R. V. GADAG and M. R. GAJENDRAGAD, *Indian J. Chem*., 1978, 16A, 703.
5. R. V. GADAG and M. R. GAJENDRAGAD, *Curr. Sci*. 1979, 48, 839.
6. T. GEORGE, R. TAMILRAMANI and D. A. DABHOLKAR, *Indian J. Chem*., 1969, 7, 959.
7. D. BANERJEA and I. P. SINGH, *Indian J. Chem*., 1968, 6, 34.
8. B. SINGH, R. SINGH, R. V. CHAUDHARY and K. P. THAKUR, *J. Indian, Chem*., 1973, 11, 174.

J. Indian Chem. Soc.,
Vol. LVII, March 1980, pp. 273-274

Synthesis and Spectral Characterization of Schiff Base Complexes of Cu(II)

O. P. ARORA* and SUDHINDRA N. MISRA

Department of Chemistry, University of Jodhpur, Jodhpur-342 001

and

M. P. BHUTRA

Department of Physics, University of Jodhpur, Jodhpur-342 001

Manuscript received 23 October 1979, accepted 30 December 1979

Six new complexes with Schiff bases derived from the *bis* (ethylacetoacetato) Cu(II) have been prepared and characterized by elemental analysis magnetic measurements electronic & I. R. Spectra. All these studies indicate that the complexes most probably have distorted octahedral structure.

A large number of metal complexes of Schiff base have been reported in literature-[1]-including those with Cu(II)[2]. We report here the result of our studies on the complexes of Cu(II) with Schiff base *bis* (vanillin) ethylenediamine, (Van-en), *bis* (Vanillin) propylenediimine (Van-pn), *bis* (Vanillin) benzidine (van-ben), *bis* Vanillin-O-phenylene diimine (Van-O-phen), Vanillin α-nephthylimine (Van-α naph); *bis* (Vanillin) thiosemi-carbazone (Van-tscz).

Experimental

All the chemicals used were of AnalaR grade Diaquo *bis* (ethylacetoacetacto) Cu(II)[3] and Schiff bases[4] were prepared as per method given in literature.

Preparation of Complexes

The addition of diaquo *bis* (ethylacetoacetato) copper(II) (0.01*M*) dissolved in the chloroform to the solution of Schiff base *bis* (Vanillin) ethylenediimine (0.01*M*) in ethanol resulted in the separation of dark yellow precipitate. The compound was filtered, washed with ether and dried in vacuum at room temperature.

In case of Schiff bases e.g. *bis* (Vanillin) propylenediimine, Vanillin-α naphthylimine and *bis* (Vanillin) O-phenylenediimine no precipitation was occured on mixing the reactants at room temperature. Hence the reaction mixture was refluxed for an hour and volume was reduced to one third. The solution thus obtained was kept for slow crystallization in dessicator. Within three to four days crystalline compound was obtained. The product was washed with ether and dried in vacco (yield 78-88%).

*For correspondence.

The compounds were found soluble in coordinating solvents e.g. dimethyl sulfoxide and dimethyl formamide while sparingly soluble in methanol and ethanol.

Analysis

Copper was estimated by standard method and nitrogen by kjeldahl method. The result of the anaysis are shown in Table 1.

Physical measurement :

The electronic spectra of all the complexes in DMF were obtained with Carl-Zeiss VSU-2 spectrophotometer. Magnetic susceptibility measurements were made in solution using Gouy method at 25°. The I. R. spectra of the complexes in KBr pellet were recorded on Perkin-Elmer 521-Spectrophotometer in the region 4000-400 cm^{-1}.

Result and Discussion

Results given in the Table-1 shows that complexes have the composition 1 : 1. The value of magnetic moment (μ_{eff}) of these complexes are in the range of 1.82-1.92 BM. Suggesting the presence of one unpaired electron and hence the complexes are spin free with octahedral stereochemistry.

The absorption spectra of the complexes is characterized by two band maxima in the region 705-740 nm and 815-865 nm (Table 1) which also supported the distorted octahedral species of Cu(II) complexes[5,6] studies on electronic spectra of Cu(II)[7] indicate that the three transitions : 2_{D_1} $\nu^2{}_{A_1}(\nu_1)\rightarrow 2A_1$ (ν_1), $2_{D_1}\rightarrow 2_{D_2}$ (ν_2), $2_{D_1}\rightarrow 2E$ (ν_3) close in energy are found, it might be due distortion caused by the non identical nature of coordinating atoms diminishing the ν_1 band.

TABLE 1—ANALYSIS, MELTING POINTS, MAGNETIC MOMENT AND ELECTRONIC SPECTRAL OF Cu(II) COMPLEXES

S. No.	Compounds	MP° (°C)	Copper calc	Copper found	Nitrogen calc	Nitrogen found	Sulpher calc	Sulpher found	µeff BM.	Electronic Spectra ν_2	Electronic Spectra ν_1
1.	$Cu(EAA)_2(Van\text{-}en)$	182 d	9.77	9.3	4.30	4.1	-	-	1.82	720 nm	825 nm
2.	$Cu(EAA)_2(Van\text{-}O\text{-}phen)$	-	9.10	8.7	4.01	4.0	-	-	1.85	705 nm	815 nm
3.	$Cu(EAA)_2(Van\text{-}ben)$	300	8.20	8.8	3.61	3.1	-	-	1.87	740 nm	865 nm
4.	$Cu(EAA)_2(Van\text{-}\alpha\ naph)(H_2O)$	140-145	10.29	9.8	2.26	2.2	-	-	1.88	735 nm	855 nm
5.	$Cu(EAA)_2(Van\text{-}Pn)$	220	9.56	9.8	4.21	4.3	-	-	1.84	725 nm	840 nm
6.	$Cu(EAA)_2(Van\text{-}tscz)$	147 d	9.32	9.3	6.16	5.8	4.70	4.9	1.92	715 nm	855 nm

TABLE 2—SIGNIFICANT I. R. VIBRATIONAL FREQUENCIES AND THEIR TENTATIVE ASSIGNMENTS

Complexes	νC=O	νC=N	νC-N	Assignment Frequency CM^{-1} νC-O	Phenolic -OH	νC-N	νC=C	νCu-N
$Cu(EAA)_2(Van\text{-}en)$	1715w	1665s	1575s	1500s	1275s	1020m	1450m	435s
$Cu(EAA)_2(Van\text{-}O\text{-}phen)$	1720w	1665s	1590s	1500s	1285s	1025s	1450w	450wbr
$Cu(EAA)_2(Van\text{-}ben)$	1720w	1675w	1585s	1495s	1285s	1025w	1445w	445m
$Cu(EAA)_2(Van\text{-}\alpha Naph)(H_2O)$	1710w	1665s	1590s	1500s	1280s	1020s	1450m	455s
$Cu(EAA)_2(Van\text{-}Pn)$	1720w	1665s	1580s	1490w	1280s	1020m	1450wbr	440m
$Cu(EAA)_2(Van\text{-}tscz)$	1705w	1665s	1580s	1495s	1280s	1020s	1460w	445w

The band attributable to Intra molecular hydrogen bonded OH has not disappeared in the complexes[8]. This indicate the OH of the ligand has not taken part in the complex formation. The elemental analysis support the above statement (Table 2).

A strong band around 1590 cm^{-1} is assigned to the C=N stretch of the free Schiff base and that found in the region 1665-1675 cm^{-1} for the complexes. This frequency Schiff suggests the coordination through the azomethine group[9].

The characteristic band due to the C=O and C=C of the *bis* (ethylacetoacetato) copper(II) found at 1600 cm^{-1} and 1525 cm^{-1} [10] respectively. Former one shifts to higher frequencies where as the latter one shifts to lower frequencies on complexation. Bands appearing in the region 1720-1450 cm^{-1} are difficult to assign as various bands fall in this region. However, the bands have been assigned tantetively comparing the spectra of respective ligand.

Metal nitrogen stretching vibration also appear in the region 455-435 cm^{-1} in all the complexes. This band either does not shift or shifts slightly on substitution in ligand. Other Cu-N bands fall beyond the range of instrument. This supports the coordination of nitrogen to metal.

The above spectral and magnetic study suggests the distorted octahedral symmetry of the complexes under study.

Acknowledgement

Authors are grateful to Prof. R.C. Kapoor, Head, Department of Chemistry, University of Jodhpur, Jodhpur for providing the facilities.

References

1. R. H. HOLM, G. W. EVERETT (JR) and A. CHAKRAVERTY, Progress in Inorganic Chemistry, edited by F. A. COTTON (Interscience, New York) 1966, 7, 83.
2. WILLIAM E. HATFIELD "Transition metal Chemistry Vol. 5 Edited by R. L. CARLIN 1969, 47.
3. R. L. BELFORD, A. E. MARTELL and M. CALVIN, *J. Inorg Nuclear Chem.*, 1956, 2, 11.
4. FAKHRUL HASAN RIZVI and NASEER AHMAD, *J. Indian Chem. Soc.*, 1975, 54, 1084.
5. J. I. BULLOCK and S. L. JOHNES, *J. Chem. Soc.*, (A) 1971, 2351.
6. NARAYAN S. BHAVE and R. B. KHARAT, *J. Indian Chem. Soc.*, 1979, 56, 244.
7. C. A. AGAMBER and K. G. ORREL, *J. Chem. Soc.*, (A) 1969, 897.
8. H. H. FREEDMAN, *J. Amer, Chem. Soc.*, 1961, 83, 2900.
9. N. S. BIRADAR and U. H, KULKARNI, *J. Inorg. Nuclear Chem.*, 1971, 33, 3847.
10. R. W. HAY and B. P. CAUGHLEY, *Aust. J. Chem.*, 1967, 20, 1829.

J. Indian Chem. Soc.,
Vol. LVII, March 1980, pp. 275-278

Synthesis and Characterization of Some Polymeric Metal-Complexes of Terephthalaldehyde *bis*-(4-Phenylthiosemicarbazone)

P. L. MAURYA, B. V. AGARWALA and ARUN K. DEY*

Chemical Laboratories, University of Allahabad, Allahabad-211 002

Manuscript received 6 September 1979, accepted 30 December 1979

Chain coordination polymeric complexes $(ML.2H_2O)_n$ (M=metal ion, L=$C_{22}H_{18}N_6S_2$ and n=degree of polymerization) between Co(II), Ni(II) of Cu(II), and terephthalaldehyde *bis*-(4-phenylthiosemicarbazone) (TPBPTS) have been synthesized, and characterized through analytical, spectral (infrared and reflectance), magnetic and thermal studies. The powdery coloured complexes are insoluble in water and in common organic solvents. Infrared spectra show that the ligand molecules act as tetradentate coordinating through the thiolo sulphur and nitrogen of the C=N group. The metal ion is the bridging unit between the donor sites of the ligand, and the polymeric chain grows through consecutive TPBPTS-metal linkages. Magnetic and electronic spectral data suggest octahedral geometry. The order of thermal stability is : Ni > Co > Cu.

THIOSEMICARBAZONES form coordination polymers[1-4] with bivalent metal ions. Some of its derivatives have been tried for applications in medicine and a significant correlation between the chelating properties and antitumor activity of a group of heterocyclic aldehydic thiosemicarbazones in animal systems has been noted[5-8]. Special attention has been paid in the context of their activity against viruses, protozoa, and small pox[9-12].

The present investigation is in continuation with the work on coordination polymers in progress in these laboratories[13-16], and describes the syntheses, general properties, composition, infrared and reflectance spectra, magnetic susceptibility measurements and thermogravimetric analyses of complexes of cobalt(II), nickel(II) and copper(II) with terephthalaldehyde *bis*-(4-phenylthiosemicarbazone) (TPBPTS).

Experimental

Materials :

TPBPTS was prepared by the method reported earlier[17]. $Co(CH_3COO)_2.4H_2O$, $Ni(CH_3COO)_2.4H_2O$ and $Cu(CH_3COO)_2.H_2O$ (all of BDH make), and the solvents used were of reagent grade.

Preparation of the complexes :

To the metal salt solution in 25 ml DMF [0.42 g of $Co(CH_3COO)_2.4H_2O$, 0.42 g of $Ni(CH_3COO)_2.4H_2O$ or 0.50 g of $Cu(CH_3COO)_2.H_2O$] 1.08 g of TPBPTS also in DMF (100 ml) was added dropwise with constant stirring. The mixture when refluxed at 130° for ca 2h, and left overnight yielded the complex, which was filtered, washed once with DMF and then with ethanol several times, till the filtrate was colourless. The product was finally washed with ether, and dried over calcium chloride in a vacuum desiccator.

Physical Characteristics :

The metal-complexes which are stable and powdery in appearance do not dissolve in water and in common organic solvents viz. ethanol, acetone, benzene, nitrobenzene, chloroform, DMF and DMSO. The colour and temperatures of decomposition are shown in Table 1.

TABLE 1—EMPIRICAL COMPOSITION AND CHARACTERISTICS OF TPBPTS-COMPLEXES

Empirical Composition	Colour	Dec. temp. (°C)	Elemental analyses %, Found (calc) Metal	C	H	N
$[Co(C_{22}H_{18}N_6S_2).2H_2O]$	reddish brown	270	11.05 (11.23)	51.42 (50.29)	4.32 (4.19)	17.05 (16.00)
$[Ni(C_{22}H_{18}N_6S_2).2H_2O]$	reddish brown	360	10.85 (11.18)	49.43 (50.31)	3.90 (4.19)	17.45 (16.00)
$[Cu(C_{22}H_{18}N_6S_2).2H_2O]$	greenish yellow	260	11.15 (11.99)	48.12 (49.85)	4.45 (4.15)	16.15 (15.86)

*For correspondence.

Elemental analysis :

Microanalytical methods were employed for the determination of carbon, hydrogen and nitrogen. The complexes were decomposed by HNO_3 and the metal contents estimated titrimetrically against EDTA.

Spectral studies :

I.R. spectra using KBr pellets were recorded with the aid of a Beckman Infrared Spectrophotometer in the range of 4000-400 cm^{-1}. Diffuse reflectance spectra in the solid state were obtained from a Spectrophotometer Model VSU-2 in the range of 200 to 900 nm.

Magnetic measurements :

The magnetic susceptibility measurements of the solid complexes were done with a Guoy set up at room temperature 25°.

Thermogravimetry :

TG data were obtained from an assembly capable of producing temperatures upto 800° with a heating rate of 10° min^{-1}.

Results and Discussion

The analytical data (Table 1) agree with the general formula$(ML.2H_2O)_n$ (where M = metal ion, $L=C_{22}H_{18}N_6S_2$ and n = degree of polymerization). The presence of water molecules is indicated by the loss in weight of the complexes on heating (Fig. 1).

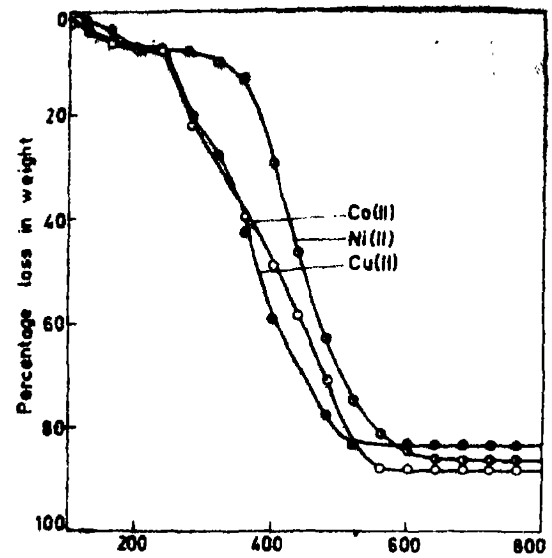


Fig. 1. Thermal stability of TPBTS-complexes

The observed weight loss is 6.85, 6.86 and 6.79% upto the temperature 240° which corresponds to the loss of $2H_2O$. The thermal stability data show that the decomposition of the complexes starts at 270°(Co), 360° (Ni) and 260°(Cu), and the complete decomposition of the organic material takes place at 550-600° leaving a residue of the metal oxide.

Table 2 shows the values of the magnetic moments, significant bands in the reflectance spectra, and the geometry of the complexes.

TABLE 2—MAGNETIC MOMENT, ELECTRONIC SPECTRA AND GEOMETRY OF THE COMPLEXES

Complex with	Magnetic moment (B.M.)*	Position of the bands (cm^{-1})	Assignments	Geometry
Co(II)	4.93	24,260	$^4T_{1g}(F) \rightarrow ^4A_{2g}(F)$	
		20,410	$^4T_{1g}(F) \rightarrow ^4T_{2g}(P)$	Octahedral
		16,000	$^4T_{1g}(F) \rightarrow ^2E_g$	
Ni(II)	2.88	26,310	$^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$	
		14,290 13,000	$^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$	Octahedral
Cu(II)	1.92	14,290	$^2E_g \rightarrow ^2T_{2g}$	Octahedral

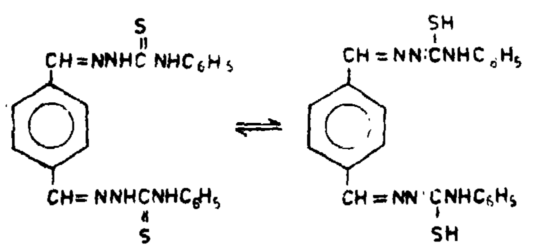
*1B.M. $= 9.273 \times 10^{-24} Am^2$

The structure of TPBPTS is represented in (I)[16]. The thione group (C=S) having protons adjacent to it is relatively unstable in the monomeric form, and tends to change over to a stable C-S single bond by enethiolization[17]. The infrared spectrum (Table 3) of TPBPTS shows an intense band at 1430 corresponding to C=S stretching vibration ; and no S-H stretching band near 2570 is observed which indicates that in solid state it remains in thione form (I). However, in solution it is likely to be in equilibrium with the thiolo tautomeric form (II).

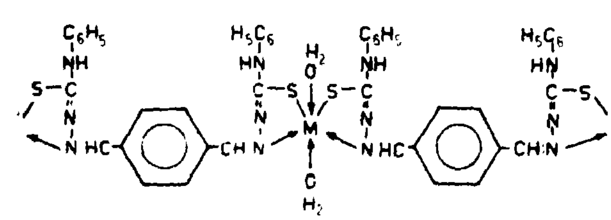
TABLE 3—BAND ASSIGNMENTS IN THE INFRARED SPECTRA OF TPBPTS AND ITS COMPLEXES (cm^{-1})

TPBPTS	Co(II)	Ni(II)	Cu(II)	assignments
...	3545 s	3550 s	3545 s	νO-H
3480 m	3485 s	3470 s	3470 s	νN-H
3440 w	3435 s	3440 w	3430 w	
3040 m	3035 m	3030 m	3040 w	νC-H
1680 vs	1700 s	1695 vs	1705 s	νC=N
	1670 vs	1680 vs	1680 s	
	1615 s	1600 s	1600 s	δH_2O
1590 vs	1590 vs	1585 s	1585 vs	νC=C &
1550 s	1540 s	1550 vs	1545 s	νC=N-N
1480 s	...	...	...	νC=S &
1430 s		...		νN-C-N
1340 vs	1340 vs	1335 vs	1325 vs	νC-N of Ar-N type
1140 s	1130 vs	1135 s	1140 vs	*p*-substituted phenyl ring
975 s	960 s	900 s	960 s	C-H out of plane
870 s	875 s	870 s	870 s	bending
750 vs	740 w	735 s	735 s	
...	630 vs	650 s	615 s	νM-N & νM-S
	535 s	540 s	540 s	
450 s	...	...	...	δN-C-N

vs=very strong, s=strong, m=medium, w=weak



I II



III. POLYMERIC TPBPTS - COMPLEX

The spectra of both ligand and the complexes show strong absorption bands near 3480 and 3440, due to N-H stretching vibration. The band at 1680 assignable to C-N stretching vibration of the free ligand shifts to higher frequency region in the cases of the complexes (an additional band is observed near 1700). The shifting of the band towards higher frequency region indicates the increase in bond order of the C=N bond, which may arise due to increase in the conjugation of *pi*-electron system. The *d*-electrons of the metal ions are back donated to the orbital of the ligand participating in conjugation[18]. The intense bands in the range of 1480 to 1430 in the spectrum of the ligand (stretching bands of N-C-N and C=S respectively), disappear in the spectra of the complexes. This appears to be due to the change in the nature of N-C-N to N-C=N and of C=S to C-S on complexation[1,4,19]. New bands near 3550 and 1600 in the complexes have been assigned to νO-H and δH_2O vibrations of the coordinated H_2O[20]. The bands in the range of 650 to 535 are due to M-N and M-S stretching vibrations (All wave numbers are expressed in cm^{-1}).

TPBPTS behaves as tetradentate chelating agent, coordinating metal ions each through the thiolo sulphur atom and the terminal nitrogen atom of the C=N group of the Schiff base. Coordination polymerization is achieved since steric factors prevent the coordination of all the donors to a single metal ion, which therefore acts as bridging unit between the donor sites of the ligand, and thus the polymeric chain grows through the consecutive TPBPTS-metal linkages (III).

The geometry of the ligand, analytical data, the extreme insolubility of the compounds and thermal stability suggest the polymeric nature of the complexes.

Acknowledgement

The work described here is a part of a project sponsored by the Ministry of Defence, Government of India, and the authors are grateful for the financial support.

References

1. D. N. Chakravarty and W. C. Drinkard, Jr., *J. Indian Chem. Soc.*, 1960, **37**, 517.
2. W. C. Drinkard, Jr. and D. N. Chakravarty, WADC, *Tech. Report*, 591/761, 1960, 232.
3. M. Murcu and M. Dima, *Rev. Roum. Chem.*, 1967, 12, 1353.
4. M. Murcu and M. Dima, *Rev. Roum. Chem.*, 1968, 13, 359.
5. M. Murcu, M. Dima and G. Rusu, Rom.. 52, 349 (Cl. CO89), 05 Oct. 1970, *Appl.* 04 Apr. 1968, 2pp; *Chem. Abs.*, 1971, 74, 126516u.
6. I. H. Krakoff, E. Etcubanas, C. Tan, K. Mayer, V. Tethune and J. H. Burchenal, *Cancer Chemotherapy Reports* Part-I, 1974, **58**, 207.
7. F. A. French, E. J. Blanz, S. C. Sadlix and J. Brockman, *J. Medicin. Chem.*, 1974, 17, 172.
8. K. C. Aggarwal, A. J. Lin, B. A. Booth, J. R. Wheaton and A. C. Sartorelli, *J. Medicin. Chem.*, 1974, 17, 631.
9. D. J. Bauer, L. S. Vincent, C. H. Kempe and A. W. Downie, *Lancet*, 1963, 20, 494.
10. H. G. Petering, H. H. Buskirk and G.E. Underwood, *Cancer Res.*, 1964, 64, 367.
11. J. A. Grim and H. G. Petering, [*Cancer Rev.*, 1967, 27, 1278.
12. N. Orlova, V. A. Aksensova, D. A. Selidovkin, N. S. Bodganova and G. N. Perskin, *Russ. Pharm. Toxicol.*, 1968, 348.
13. P. L. Maurya, B. V. Agarwala and A. K. Dey, *Inorg. Nuclear Chem. Lett.*, 1977, 13, 145.
14. P. L. Maurya, B.V. Agarwala and A. K. Dey, *Indian J. Chem.*, 1978, 16A, 358.
15. V. Banerjie and A. K. Dey, *Makromol. Chem.*, 1979, 180, in press.
16. P. L. Maurya, B. V. Agarwala and A. K. Dey, *J. Indian Chem. Soc.*, 1978, 55, 418.
17. R. Mayer, *Organosulphur Chemistry*, Interscience, New York, 1967, pp. 219.
18. K. Burger, I. Ruff and F. Ruff, *J. Inorg. Nulcear Chem.*, 1965, 27, 179.
19. M. A. Ali and R. Bose, *J. Inorg. Nuclear Chem.*, 1977, 39, 265.
20. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, John Wiley and Sons, New York, 1970, pp. 166.

J. Indian Chem. Soc.,
Vol. LVII, March 1980, pp. 279-281

Complexes of Some Bivalent Metals with Substituted Triazole and Thiadiazole Derivatives

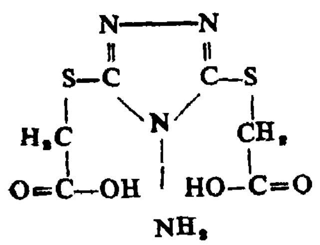
B. N. KESHARI and L. K. MISHRA

Department of Chemistry, Patna University, Patna-800 005

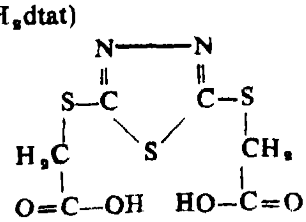
Manuscript received 22 August 1979, accepted 30 December 1979

The complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with 3,5-dicarboxymethylthio-4-amino-4, 1,2-triazole and 2,5-dicarboxymethylthio-1,3,4-thiadiazole of the general formula $ML.nH_2O$ (n = 1, 2 or 3) have been prepared and characterised by UV, IR and magnetic susceptibility measurement. The spectral parameter 10Dq, B and *β* of the octahedral complexes of nickel(II) and cobalt(II) have been calculated.

THE complex compounds of 4-amino-3, 5-dimercapto-1, 2, 4-triazole and 2, 5-dimercapto-1, 3, 4-thiadiazole have been reported earlier from this laboratory[1] and by other workers[2-4]. 3, 5-Dicarboxymethylthio-4-amino-4, 1, 2-triazole (H_2dtat) and 2, 5-dicarboxymethylthio-1, 3, 4-thiadiazole (H_2dtth) are multidentate ligands possessing nitrogen, sulphur and carboxylic oxygens as potent donor sites. The complexing behaviour of these ligands does not appear to be reported in literature hitherto. In present communication we are reporting the complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with these ligands.



(H_2dtat)



(H_2dtth)

Experimental

All chemicals and solvents used were either E. Merck extra pure or BDH (A.R.) quality and used without further purification. The ligand was prepared as described elsewhere[5].

Preparation of complexes: $ML.nH_2O$($M = Mn^{2+}$, Ni^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} ; LH = H_2dtth and H_2dtat and n = 1, 2 or 3).

Hydrated metal acetate (0.01 mole dissolved in 30-40 ml of methanol) were mixed to a hot methanolic solution of ligand (0.01 mole) and refluxed on a steam bath for about 15 minutes. The complexes either separated out immediately or on cooling the refluxate at room temperature. The products were washed with methanol and ether and dried in air. The colour, analytical results and magnetic moment values of the complexes are given in Table 1.

TABLE—1

Compounds	Colour	% of Metal		% of Nitrogen		% of Carbon		% of Hydrogen		μ_{eff}
		Found	Reqd.	Found	Reqd.	Found	Reqd.	Found	Reqd.	(BM)
$[Ni(dtat)(H_2O)_2]H_2O$	Light blue	15.43	15.65	14.78	14.93	19.19	19.20	1.61	1.60	3.54
$[Ni(dtth)(H_2O)_2]H_2O$	Light blue	15.45	15.59	7.29	7.43	19,13	19.11	1.06	1.06	3.32
$[Co(dtat)(H_2O)_2]H_2O$	Pink	15.69	15.73	14.85	14.93	19 20	19.19	1.62	1.60	5.12
$[Co(dtth)(H_2O)_2]H_2O$	Pink	15.40	15.65	7.58	7.43	19.15	19.10	1.05	1.06	4.85
$[Mn(dtat)(H_2O)_2]H_2O$	Pinkish white	14.97	14.79	14.98	15.09	19.80	19.85	1.62	1.61	6.08
$[Mn(dtth)(H_2O)]$	Pinkish white	16.37	16.30	8.32	8.31	21.39	21.37	1.20	1.18	5.84
$[Cu(dtat)].2H_2O$	Green	17.45	17.55	15.58	15.49	19.95	19.90	1.68	1.66	1.92
$[Cu(dtth)].2H_2O$	Green	17.36	17.46	7.79	7.70	19.75	19.81	1.15	1.10	1.82
$[Cd(dtat)].2H_2O$	White	27.80	27.78	13.58	13.63	17.60	17.53	1.43	1.40	Dia.
$[Cd(dtth)].2H_2O$	White	27.57	27.67	6.89	6.79	17.50	17.46	1.00	0.96	Dia.
$[Zn(dtat)].H_2O$	White	19.03	18.91	16.21	16.20	20.91	20.83	1.75	1.73	Dia.
$[Zn(dtth)].2H_2O$	White	17.86	17.88	6.70	7.66	19.75	19.70	1.10	1.09	Dia.

Physical Measurements :

The magnetic susceptibility of the complexes were determined by Gouy method[6], reflectance spectra recorded on Hilger Watt UV spectrophotometer No.H-700 in the range of 350-1000 nm and IR spectra were recorded on Perkin Elmer 237 spectrophotometer.

Results and Discussion

From the results of elemental analyses, it is found that H_2dtth and H_2dtat exhibit their dibasic behaviour and form neutral complexes of composition M(dtth).nH_2O and M(dtat). nH_2O (n = 1, 2 or 3) with bivalent zinc, cadmium, cobalt, copper, nickel and manganese.

The hydrated complexes on heating at 120°, either remain uneffected or partially lose water molecules without appreciable change in colour. This indicates that the water molecules which are lost below 120° are probably lattice water but those are retained, are most likely the coordinated water. Thus, considering the usual coordination number 6 for Co^{2+}, Mn^{2+}, Cu^{2+} and Ni^{2+}, it is presumed that H_2dtth is bonded as quadridentate ligand with Co^{2+}, Mn^{2+}, Ni^{2+} and Cu^{2+} in complexes M(dtth). nH_2O. In case of complexes M(dtat). nH_2O (M = Co^{2+}, Ni^{2+}, Mn^{2+} and Cu^{2+}), the ligand is also quadridentate, forming bridges between two metal atoms.

Magnetic moments and electronic spectra :

The room temperature magnetic moment values of the complexes of Ni^{2+} (μ_{eff} = 3.09—3.19 BM), Co^{2+} (4.85—5.12 BM) and Mn^{2+} (5.84—6.08 BM) are straight forward and fall in the range of high spin octahedral complexes of respective metal ions[7]. Copper (II) complexes display magnetic moment values in the range of 1.82—1.92 BM, similar to magnetically dilute copper (II) complexes[8]. As expected, the zinc (II) and cadmium (II) complexes are diamagnetic.

The electronic reflectance spectra of Zn^{2+}, Cd^{2+} and Mn^{2+} complexes do not exhibit electronic bands in the range 28500—10000 cm^{-1}. The medium to weak reflectance bands of complex [Ni(dtth) $(H_2O)_2$] H_2O and [Ni(dtat)$(H_2O)_2$] H_2O at 25000 and 15385—14705 cm^{-1} are attributed to ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transitions in octahedral ligand field. The values of 10Dq, B′ and β(Table 2) calculated from the relation of ν_2 and ν_3 transitions[9,10] indicate that ligand produces weak field around nickel (II) atom. The copper (II) complexes Cu(dtth). 2H_2O and Cu(dtat). 2H_2O display strong and asymmatric band in the region 15385—12195 cm^{-1} assignable to combination of ${}^2B_{1g} \rightarrow {}^2B_{2g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ transition[11,12] and another shoulder near 27027cm^{-1} (probably charge transfer type). The medium and asymmetric band of Cu(dtth). 2H_2O on the higher energy range 15385—12902 cm^{-1} indicates a lower degree of distortion from octahedral environment in the complex. Both cobalt(II) complexes display two ligand field reflectance bands near 22000 sh and 19000 cm^{-1} (strong) assignable to ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ and ${}^4T_{1g} \rightarrow {}^4A_{2g}(F)$ transition, though the latter transition is generally not observed in octahedral cobalt(II) complexes[13]. The second band has probably gained intensity due to tetragonal distortion of cobalt(II) ion. The value of 10Dq, B′ and β (Table-II) computed from the relations of ν_2 and ν_3 transition of solid complexes fall in the range of octahedral environment of ligand atoms around cobalt(II) ions[13].

TABLE 2—ELECTRONIC SPECTRAL BANDS, THEIR PROBABLE ASSIGNMENTS AND CRYSTAL FIELD PARAMETERS

Complexes	Band position (cm^{-1})	Assignment	10 Dq (cm^{-1})	B′ (cm^{-1})	β	ν_1 (cm^{-1})
[Co(dtat)$(H_2O)_2$].H_2O	19230	${}^4T_{1g}$—${}^4A_{2g}$	10247	967	0.99	8983
	22222	${}^4T_{1g}$ - ${}^4T_{1g}(P)$				
[Co(dtth)$(H_2O)_2$].H_2O	19607	${}^4T_{1g}$ - ${}^4A_{2g}$	10690	925	0.95	8917
	21739	${}^4T_{1g}$ - ${}^4T_{1g}(P)$				
[Ni(dtat)$(H_2O)_2$].H_2O	15385	${}^3A_{2g}$—${}^3T_{1g}(F)$	9456	788	0.75	9456
	25000	${}^3A_{2g}$ - ${}^3T_{1g}(P)$				
[Ni(dtth)$(H_2O)_2$].H_2O	14705	${}^3A_{2g}$ - ${}^3T_{1g}(F)$	9163	833	0.79	9163
	25000	${}^3A_{2g}$—${}^3T_{1g}(P)$				
[Cu(dtat)].2H_2O	13890-12195	${}^2B_{1g}$—${}^2B_{2g}$ ${}^2E_g$	-	-	-	-
[Cu(dtth)].2H_2O	26666	C—T				
	15385-12902	${}^2B_{1g}$—${}^2B_{2g}$ ${}^2E_g$	-	-	-	-

IR spectra :

From the studies of a systematic shift in the IR spectral bands of 2, 5-dicarboxymethylthio-1, 3, 4-thiadiazol and 3, 5-dicarboxymethylthio-4-amino-1, 2, 4-triazole in their complexes, bonding of the ligand molecules has been suggested.

Free ligands display a number of bands in 3-3.5 μ region attributable to $\nu(NH_2)$, ν_s (CH_2), $\nu_{as}(CH_2)$ and ν (OH) vibrations. Medium bands observed at 2720 and 2605 cm^{-1} in the IR spectra of H_2dtat and 2700 and 2580cm^{-1} in the IR spectra of H_2dtth are attributed to H-bonded (COOH) group. These bands disappear in the IR spectra of metal complexes supporting the coordination of ligand by deprotonation of carboxylic OH.

The IR spectrum of H_2dtat displays strong bands at 3350 and 3210 cm^{-1} which are shifted to lower wave numbers in its complexes. These bands are assigned to NH asymmetric and symmetric vibration of NH_2 group. The shift of the ν(NH) vibrations suggest the bonding of NH_2 group in H_2dtat complexes. The ν_{as}(COO) vibration of H_2dtat and H_2dtth is observed as broad and very strong band at 1700 cm^{-1} (H_2dtat) and 1690—1730 cm^{-1} in case of H_2dtth[14]. In complexes the ν_{as} (COO) is shifted to lower frequencies and observed as broad band near 1590—1640 cm^{-1}. The ν_s (COO) is observed at 1300—1305 cm^{-1} in free ligands which is shifted to higher frequencies in their complexes and observed at 1360—1400 cm^{-1}. From the shift in ν_{as}(COO) and ν_s (COO) vibration, it is inferred that both carboxyl oxygen is involved in bonding[16-17]. It appears that one of carboxylic oxygen is bonded to water molecules present in the complexes while the second one is bonded to metal atoms. The δ (NH_2) band of H_2dtat is observed at 1640 cm^{-1} but in complexes it is lenve oped in strong ν_s (COO) vibration.

In the region 1450—750 cm^{-1} free ligands display a number of bands attributable to δ (OH) and CH_2 deformation, ν(C—N), ν(C—C) CH_2 wagging, CH_2 rocking, ν(C—O) and ν(C=S) vibrations. These vibrations are not well resolved and sharp in the complexes. The IR spectra of H_2dtth exhibits a medium band at 750 cm^{-1} which is shifted to lower frequency and observed near 700$\pm$20 cm^{-1} suggesting that thiosulphur of H_2dtth are involved in coordination. In case of uncoordinated H_2dtat, a number of weak bands could be observed in the region 800—700 cm^{-1} and therefore no definite position of ν(C—S) band either in free ligand or its complexes could be ascertained. But from analogy the coordination of ether sulphurs may also be suggested in its complexes.

References

1. B. K. Sinha, R. Singh, J. P. Srivastava and L. K. Mishra, *J. Inorg. Nuclear Chem.*, 1977, **39**, 1797.
2. M. R. Gajendragad and U. Agarwala, *Z. anorg. allgem. Chem.*, 1975, **415**, 84.
3. M. R. Gajendragad and U. Agarwala, *Indian J. Chem.*, 1975, 13, 697.
4. M. R. Gajendragad and U. Agarwala, *Aust. J. Chem.*, 1975, **28**, 1529.
5. J. Sandström, *Acta Chem. Scand.*, 1961, **15**, 1295.
6. B. N. Figgis and J. Lewis, "Modern Coordination Chemistry", edited by J. Lewis and R. G. Wilkins, Interscience Publishers, New York, 1960, p. 403.
7. R. S. Nyholm and B. N. Figgis, *Prog. Inorg. Chem.* Ed. F. A. Cotton, 1964, **6**, 41.
8. M. Kato, H. B. Jonassen and J. C. Fanning, *Chem. Rev.*, 1964, **64**, 99.
9. E. König, "Structure Bonding", 1971, **9**, 175.
10. D. K. Rastogi, K. C. Sharma, S. K. Dua aud M. P. Teotia, *J. Inorg. Nuclear Chem.*, 1975, **37**, 685.
11. P. Stenson, *Acta Chem. Scand.*, 1969, **23**, 1514.
12. S. J. Gruber, C. M. Harris and E. Sinn, *J. Inorg. Nuclear Chem.*, 1968, **30**, 1805.
13. R. L. Carlin, "Transition metal Chemistry", Ed. R. L. Carlin, Vol. I, page, I, Marcel Dekkar Inc., New York, 1965.
14. L. J. Bellamy, "The infrared Spectra of Complex Molecules", John Wiley and Sons, INC., 1960, p. 159.
15. C. Duval, H. Gerding and J. Lecompte, *Rec. trav. Chem.*, 1950, **69**, 391.
16. M. J. Schmetz, I. Nakagawa, S. Muzushima and J. V. Quagliano, *J. Amer. Chem. Soc.*, 1959, **81**, 287.
17. E. Ellis and H. Pyszora, *Nature*, 1958, **181**, 181.

J. Indian Chem. Soc.,
Vol. LVII, March 1980, pp. 282-285

Polarographic Studies on Electrode Kinetics and Formation Constants of the Complexes Formed by In(III) and Eu(III) with Quinolinate Ions

S. K. BHASIN and OM PARKASH

Chemistry Department, M.L.N. College, Yamuna Nagar, Haryana

Manuscript received 12 October 1979, accepted 20 December 1979

The reduction of In(III) and Eu(III) in $NaClO_4$ ($\mu = 1.5$) at d.m.e. is found to be quasireversible, but it becomes reversible in the presence of quinolinate ions in case of Eu(III). The $E^r_{\frac{1}{2}}$ values for the simple Eu(III) ion and for In(III)-Quinolinate system are calculated from the observed $E_{\frac{1}{2}}$ values by Gelling's treatment and from it the kinetic parameters have been calculated. The formation constants have been calculated by DeFord and Hume method. In both systems four complex species are formed. In(III) forms stronger complex species as compared to Eu(III). The percentage distribution of the various species present in both the systems is calculated.

In(III) and Eu(III) form complexes with a number of ligands but the reduction are not reversible at d.m.e. and hence the formation constants could not be calculated from observed half-wave potentials. With the development of Koryta's[1], Matsuda's[2] and Gelling's[3] methods for quasireversible reduction, the reversible half-wave potentials ($E^r_{\frac{1}{2}}$) can be obtained from the C-V curves and thus the formation constants can be calculated.

By applying foregoing methods, the polarographic studies of the complexes formed by Eu(III) with CDTA have been carried out by Jain and Gaur[4] and with some aromatic substituted acids by Anand Kumar[5]. Recently, Eu(III) complexes with crotonate, itaconate, citraconate, 6 amino hexanoate, gluconate and 2 furoate ions have been polarographically studied by the authors [6,7].

In(III) forms complexes with various ligands; six thiocyanate complex species of In(III) have been reported[8]. Polarographic studies on the electrode kinetics and formation constants of the complexes formed by In(III) with 1 : 2 Diaminocyclohexanetetraacetic acid (CDTA)[9] and with aspirin[10] have been carried out. Recently the electrochemical behaviour of In(III) complexes with crotonate ion and gluconate[11] ions at DME has been investigated. The authors have reported[12] In(III) complexes with α-picolinic acid also.

The present paper deals with the determination of kinetic parameters and formation constants of the complexes of Eu(III) and In(III) with quinolinate ions.

Experimental

A manual polarographic set up was used for obtaining C-V curves. The DME having the characteristics m = 1.7645 mgm/sec. and t = 3.64 sec. (open circuit) was used. Sodium salt of quinolinic acid was used as the complexing agent. The polarograms were recorded after deaeration (20-25 minutes) with nitrogen. All the measurements were carried out at 30±0.1° maintained by a Haaketype ultra-thermostat. Solution containing 0.5 mM Eu(III) and In(III) and different amounts of complexing agents were prepared. The ionic strength was kept at 1.5 by adding the requisite amount of sodium perchlorate solution. An H-type cell with an agar-agar plug saturated with sodium chloride served as electrolytic cell.

Results and Discussion

A single well-defined reduction wave appeared in each case. Plots of i_d vs $\sqrt{h}$ and i_d vs metal ions-concentration were straight lines passing through the origin, showing that the reductions are controlled by diffusion. The half-wave potentials shifted to more negative values and i_d was found to decrease with increasing concentration of the ligand indicating complex formation.

In(III)-Quinolinate system

The plots of log i/i_d-i vs $E_{d.e.}$ were linear but slopes come to be of the order of 25±1 mV, which is higher than the required for three electron reduction. Therefore, the reversible half-wave potentials were determined by modified Gelling's

method [8,13] from the observed $E_{\frac{1}{2}}$ values by plotting $\left[E - \frac{RT}{nF}\log\frac{i_d-i}{i}\right]$ vs 'i' and by extrapolating i=o (Fig.1). The standard rate constant, K_s, and transfer coefficient, α, have been calculated from the plots of log (Z-1) vs ($E - E^r_{\frac{1}{2}}$), which results to straight line (Fig. 2). The value of K_s was found to be of the order of 10^{-4} cm/sec. which confirms that the electrode process is quasi-reversible in all cases.

The $E^r_{\frac{1}{2}}$ vs -log C_X plots were smooth curves in all cases showing the existence of two or more complexes in equilibria. The overall stability constants were calculated by the DeFord and Hume[14,15] treatment. The details of the method have been explained in an earlier paper [16].

The plots of F_j [(X)] vs C_X to zero ligand concentration (Fig.3) showed the presence of four complex species: [In(quinolinate)]$^+$, [In(quinolinate)$_2$]$^-$, [In(quinolinate)$_3$]$^{-3}$ and [In(quinolinate)$_4$]$^{-5}$ with $\beta_1=3\times10^6$, $\beta_2=4\times10^7$, $\beta_3=33\times10^7$ and $\beta_4=100\times10^7$ respectively. The polarographic characteristics, F_j([X]) functions and kinetic parameters have been summarised in Table 1. The percentage distribution of In(III) in various forms has been shown in Fig.4.

Eu(III) Quinolinate system :

Again the plots of log i/i_d-i vs $E_{d.e.}$ were found to be linear, but the slope for simple metal ion was 90mV, whereas the value reduces to 60 ± 2 mV in presence of quinolinate ion. Thus the electrode reaction is not reversible in case of simple metal ion

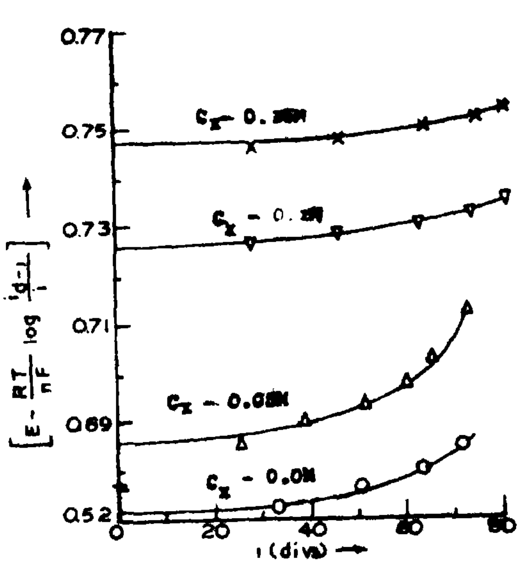


Fig. 1. Plots of i vs $\left[E - \frac{RT}{nF}\log\frac{i_d-i}{i}\right]$ For In (III)—Quinolinate system

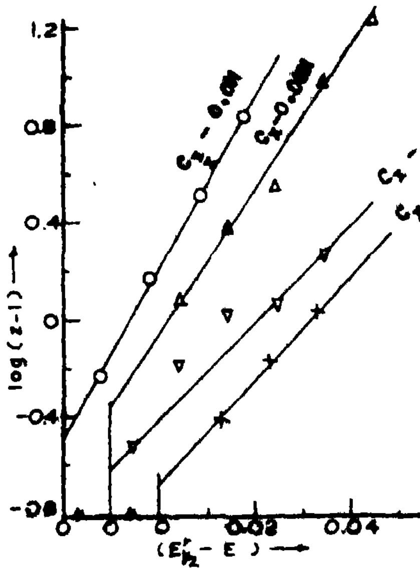


Fig. 2. Plots of log (z-1) vs $\left(E^r_{\frac{1}{2}} - E\right)$ For In(III)—Quinolinate system

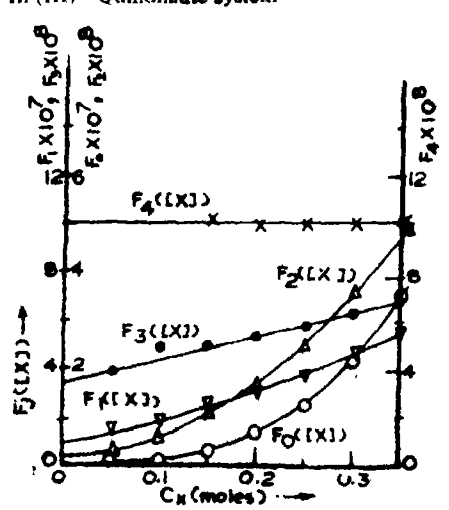


Fig. 3. Plots of Fj([X]) v Cx For In(III)-Quinolinate system

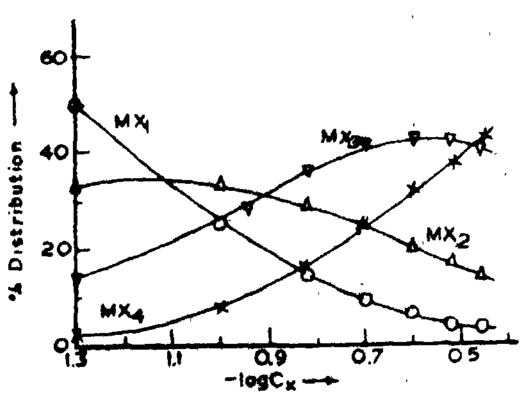


Fig. 4. Plots of % distribution vs – logCx For In(III)-Quinolinate system

TABLE 1—ANALYSIS OF POLAROGRAPHIC CHARACTERISTICS, Fo ([X]) SUNCTIONS AND KINETIC PARAMETERS FOR In(III) QUINOLINATE SYSTEM

C_X (Moles)	$E_{\frac{1}{2}}$ (-V vs SCE.	$E^r_{\frac{1}{2}}$	i_d (μ.A.)	$F_0(X)$ x 10^{-7}	α	λ (sec.$^{-1}$)	$D^{\frac{1}{2}}$ x 10^{3} (cm^2/sec.)	K_s x 10^{3} (cm/sec.)
0.00	0.5250	0.622	7.598	—	0.334	1.788	4.60	8.227
0.05	0.6855	0.686	7.462	0.030	0.375	1.357	4.53	6.146
0.10	0.7070	0.704	7.416	0.119	0.394	1.558	4.50	7.000
0.15	0.7190	0.716	7.416	0.312	0.474	1.488	4.50	7.000
0.20	0.7280	0.726	7.402	0.642	0.592	2.357	4.52	10.655
0.25	0.7355	0.734	7.402	1.234	0.524	2.645	4.52	11.955
0.30	0.7425	0.741	7.280	2.164	0.592	2.357	4.42	10.419
0.35	0.7480	0.747	7.180	3.518	0.575	2.706	4.30	11.553

TABLE 2—POLAROGRAPHIC CHARACTERISTICS AND F_j ([X]) VALUES FOR Eu(III)-QUINOLINATE SYSTEM AT 30°C (μ—1.5)

C_X (Moles)	$E_{\frac{1}{2}}$ (-V vs SCE)	i_d (Divs.)	F_o ([X]) x10^{-1}	F_1([X]) x10^{-3}	F_2([X]) x10^{-4}	F_3([X]) x10^{-4}	F_4([X]) x10^{-1}
0.00	0.6635*	93.0	—	—	—	-	-
0.05	0.7500	85.0	0.507	10.134	16.63	—	—
0.10	0.8055	82.0	4.429	44.290	42.29	-	-
0.15	0.8420	80.5	18.300	122.000	80.00	266.67	944.47
0.20	0.8655	80.0	40.820	204.100	101.05	305.25	900.00
0.25	0.8800	80.0	79.200	316.800	125.92	343.68	874.72
0.30	0.8960	80.0	146.300	487.670	168.89	406.30	937.67
0.35	0.9080	79.0	234.800	670.860	191.10	431.71	876.30

*$E_{\frac{1}{2}}$ $-Er_{\frac{1}{2}}$

but it becomes reversible by the addition of quinolinate ions. This has been confirmed by Gelling's method as shown in Fig. 5.

The kinetic parameters for the simple metal ion Eu(III) in 1.5 *M* $NaClO_4$ were calculated. The diffusion coefficient for Eu(III) comes to 5.43×10^{-6} cm²/sec. The value of K_s and α come to 2.67×10^{-4} cm/sec. and 0.81 respectively, confirming the quasi-reversible nature of the electrode process in the absence of ligand.

The plot of $E_{\frac{1}{2}}$ vs -log C_X was found to be straight line, showing the formation of two or more complex species. The plots of F_j ([X]) vs C_X to zero ligand concentration showed the presence of four complexes : [Eu(quinolinate)]$^+$, [Eu(quinolinate)$_2$]$^-$, [Eu(quinolinate)$_3$]$^{-3}$ and [Eu(quinolinate)$_4$]$^{-5}$ with $\beta_1 = 2 \times 10^3$, $\beta_2 = 40 \times 10^4$, $\beta_3 = 125 \times 10^4$ and $\beta_4 = 900 \times 10^4$ respectively. The polarographic characteristics and F_j ([X]) values have been included in Table 2. The distribution of Eu(III) in its various forms is presented in Fig. 6.

It is evident that the complexes of quinolinate ion with In(III) are much stronger than those with Eu(III). Since all the reductions are found to be diffusion controlled, Eu(III) and In(III) can be estimated polarographically in the persence of quinolinate ions.

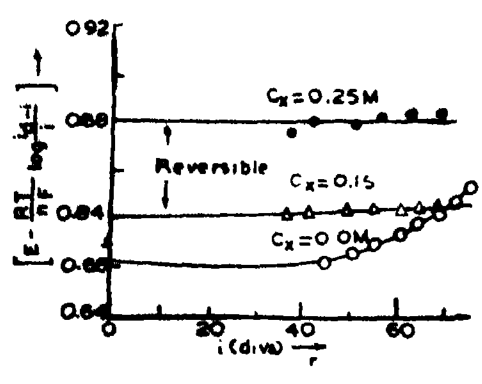


Fig. 5. Plots of i vs—$\left[E - \frac{RT}{nF} \log \frac{id-i}{i} \right]$ For Eu(III)—Quinolinate system

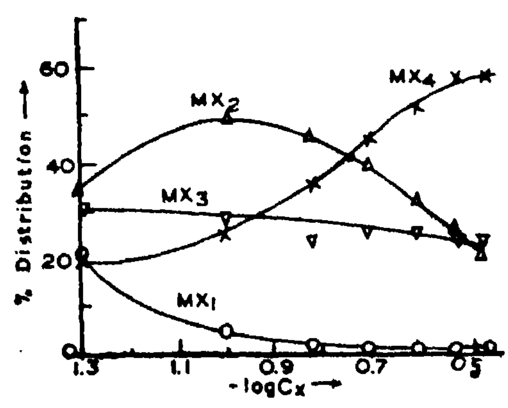


Fig. 6. Plots of % distribution vs - logCx For Eu(III)—Quinolinate system

Acknowledgement

Thanks are due to Dr. J. N. Gaur and Dr. D. S. Jain, Chemistry Department. Univetsity of Rajasthan, Jaipur for their valuable suggestions and encouragement.

References

1. J. KORYTA, *Chem., Zvesti.*, 1954, **8**, 644.
2. H. MATSUDA, *Z. Electrochem.* 1958, **62**, 977 ; 1958, **63**, 1164 and 1961, **65**, 482.
3. P. J. GELLING, *Z. Electrochem. Ber. 'Bunsenger* ; 11, Schaft, *Phy. Chem.*, 1962, **66**, 477 and 1963, 789, **66**, 167.
4. D. S. JAIN and J. N. GAUR, *Acta Chimica. Acad. Sci. Hungaricae Tomus*, 1966, *49*, 217.
5. ANAND KUMAR : Ph.D. Thesis, Rajasthan University, Jaipur, 1972.
6. OM PARKASH : Ph.D. Thesis, Rajasthan University, Jaipur, 1977.
7. S. K. BHASIN, Ph.D. Thesis, Rajasthan University, Jaipur, 1977.
8. T. P. RADHA KRISHNAN and A. K. SUNDARAM, *J. Electroanalyt. Chem.*, 1963, **5**, 124.
9. J. N. GAUR and D. S. JAIN, *Trans. Soc. Advan. Electrochemical Sci. and Techn.*, Vol. I. No. Jan. 1 1966.
10. J. N. GAUR, D. S. JAIN and M. M. PALRECHA, *J. Chem. Soc.* (A), 1968, 2201-4.
11. OM PARKASH, S. K. BHASIN, D. S. JAIN and J. N. GAUR, *Journal of the Less Common Metals*, 1978, **60**, 179.
12. D. S. JAIN, OM PARKASH and S. K. BHASIN, *J. Electrochem. Soc. India*, 1976, **25**, 139.
13. R. TAMAMUSHI and N. TANAKA, *Z. Phy. Chem.*, 1963, **39**, 117.
14. D. D. DEFORD and D. N. HUME, *J. Amer. Chem. Soc.*, 1951, **73**, 5321.
15. H. IRVING, "Advances in Polarography", 1960, 1, 42.
16. M. M. PALRECHA and J. N. GAUR, *J. Inorg. Nuclear Chem.* 1970, **32**, 1375.

J. Indian Chem. Soc.,
Vol. LVII, March 1980, pp. 286-288

Magnetic and ESR Studies on Mn(II) and Fe(III) Chelates of 1-(2-pyridylazo)-2-naphthol and 1-(2-pyridylazo)-2-phenanthrol

YUDHVIR K. BHOON, K. B. PANDEYA and R. P. SINGH

Department of Chemistry, University of Delhi, Delhi-110 007, India

Manuscript received 9 August 1979, accepted 30 December 1979

Manganese(II) and Iron(III) complexes of 1-(2-pyridylazo)-2-naphthol (PAN) and 1-2-pyridylazo)-2-phenanthrol (PAPL) have been prepared and characterized by magnetic susceptibility and ESR spectral measurements. Sextet ground state for manganese(II) complexes and doublet ground for iron(III) complexes have been inferred.

THE present communication describes preparation and characterization of Mn(II) and Fe(III) complexes of 1-(2-pyridylazo)-2-naphthol (PAN) and 1-(2-pyridylazo)-2-phenanthrol (PAPL). 2-Pyridylazo compounds have recently emerged out as an important class of chromogenic reagents[1], but very little work has been done on the structural aspects of their metal chelates[2-6].

Experimental

(a) *Preparation of ligands* :

PAN was prepared by diazotization of 2-aminopyridine with butyl nitrite (freshly prepared from 1-butanol and sodium nitrite), followed by coupling of the isolated sodium diazitate with 2-napthol in ethanol. The crude product was purified by recrystallization from ethanol.

PAPL[6] was prepared by the condensation of pyridylhydrazine with 2, 10 phenanthraquinone in acidic medium and precipitated by neutralization with aqueous ammonia (1 : 1). It was then recrystallised from dry benzene.

Preparation of complexes :

(*i*) *Manganese(II)-complexes*—15 ml of 0.1*M* aqueous solution of $MnCl_2.6H_2O$ was added to an ethanolic soiution of the ligands (750 mg of PAN or 900 mg of PAPL in 500 ml ethanol). *p*H of the solution was raised to 10.0 by adding sodium hydroxide solution. The contents were refluxed on a water-bath for about two hours, when intense pink colour developed. On concentration the complexes separated out as crystalline granules. The same were filtered, washed successively with water, ethanol and acetone and dried in an electric oven at 60°.

(*ii*) *Iron(III)-complexes*—15.0 ml 0.1*M* $Fe(ClO_4)_3$ solution was added to the ethanolic solution of ligands (750/900 mg of PAN/PAPL) and the contents were refluxed for two hours. On concentration, the complex separated out as brown powder. These were worked out as in the case of manganese(II) complex. Results of elemental analysis are presented in Table 1.

All the complexes are insoluble in water and

TABLE 1—ELEMENTAL ANALYSIS DATA

Complex	*p*H of isolation	Colour	m.p. °C	% M Calcd. (found)	% C Calcd. (found)	%N Calcd. (found)	% H Calcd. (found)
$Mn(C_{15}H_{10}N_3O)$	10.0	Pink	300	9.89 (9.99)	65.20 (65.24)	15.14 (15.24)	3.59 (3.63)
$Mn(C_{19}H_{12}N_3O)$	10.0	Pink	300	7.90 (8.00)	65.21 (66.42)	12.01 (12.24)	3.98 (4.07)
$Fe(C_{15}H_{10}N_3O)_2ClO_4.2H_2O$	3.0	Brown	300	8.12 (8.12)	52.04 (52.37)	12.32 (12.40)	3.40 (3.49)
$Fe(C_{19}H_{12}N_3O)_2ClO_4.2H_2O$	3.0	Brown	300	6.92 (7.09)	57.46 (57.92)	10.68 (10.66)	3.55) (3.55

dissolve in the common organic solvents viz., chloroform, pyridine, dimethylformamide and nitrobenzene.

Physical measurements :

The ESR spectra of the complexes as powdered samples or as pyridine solution were recorded on an X-Band Varian V-4502-12 EPR spectrometer. The low-temperature magnetic susceptibility measurements were carried out on a Gouy Balance using mercuric tetrathiocyanate cobaltate(II) as calibrant.

Results and Discussion

Manganese(II) complexes :

Mn(II)-PAN and Mn(II)-PAPL complexes show magnetic moments of 6.31 B. M. and 6.48 B. M. respectively (Table 2) indicating sextet ground state[5-6]. The higher magnetic moment values may be attributed to cooperative phenomena.

The EPR Spectrum of Mn(II)-PAN complex (solid) shows one almost symmetric signal centred around $g = 2.00$. A similar but narrower signal is obtained from pyridine solution. Mn(II)-PAPL complex on the other hand gives in solid state a spectrum indicative of the presence of zero field splitting and hence of ligand field component of very low symmetry. Further, in the spectrum of the pyridine solution, of the complex, the zero field splitting phenomenon is not observed. These observations indicate larger asymmetry in Mn(II)-PAPL complex than in Mn(II)-PAN complex. May be that PAN in its complex with manganese(II) coordinates through all the three coordination centres viz., the heterocyclic nitrogen, the nitrogen of the azo group farthest from pyridine ring and the hydroxyl group, while PAPL acts as a bidentate ligand, coordinating through the oxygen of the hydroxyl group and the nitrogen of the azo group nearer to the phenanthrene ring, the axial positions being occupied by the water molecule. In pyridine solution, the solvent molecules replace the water molecules from the axial postions and the resulting ligand field assumes almost the same symmetry as obtained from two terdentate PAN molecules. The EPR parameters have been calculated and are summarised in Table 3. Zero field splitting parameter for the Mn(II)-PAPL complex (in solid state) comes out to be 0.082 cm^{-1}.

Iron(III) complexes :

Results of magnetic susceptibility measurements on the complexes are given in Table 2. χ_M' vs. T curve for Fe(III)-PAPL is shown in Fig. 1. Curie Weiss law for the complex is obeyed ($\theta = -18°K$) and temperature independent moment of 2.00 B.M. is observed. A doublet ground state is indicated. For low-spin octahedral complexes with ground term $^3T_{2g}$, the magnetic moment values higher than spin-only values upto 2.5 B. M. are expected. The magnetic moment could be temperature dependent because of the spin orbit coupling interaction and

TABLE 2—MAGNETIC SUSCEPTIBILITY DATA

Complex	Temp. °K	$\chi_g \times 10^6$ (c.g.s.)	$\chi_M \times 10^6$ (c.g.s.)	$\chi_M \times 10^6$ (c.g.s)	μ_{eff} (B.M.)
$Mn(PAN)_2$	295.0	28.17	16540.0	16867.0	6.31
$Mn(PAPL)_2 2H_2O$	294.0	25.17	17420.0	17121.0	6.48
$Fe(PAN)_2ClO_4 2H_2O$	293.0	2.004	1378.0	1737.0	2.023
$Fe(PAL)_2ClO_4 2H_2O$	295.0	1.738	1372.0	1805.0	2.06
	206.0	2.794	2200.0	2633.0	2.08
	174.8	3.166	2494.0	2827.0	1.99
	153.7	3.714	2924.0	3357.0	2.03
	121.5	4.599	3622.0	4055.0	1.98
	110.0	5.148	4054.0	4487.0	1.99
	87.5	5.478	4313.0	4746.0	1.92

TABLE 3—EPR PARAMETERS

Complex	Medium	g	66 Zero field splitting (gauss)	(cm^{-1})
$Mn(PAN)_2$	Powder	2.00	—	—
$Mn(PAN)_2$	Pyridine	2.00	—	—
$Mn(PAPL)_2$	Powder	2.00	819.8	0.82
$Mn(PAPL)_2$	Pyridine	2.02	—	—
Complex	**Medium**	**g**		**g**
$Fe(PAN)_2ClO_4.2H_2O$	Powder	2.22		1.96
$Fe(PAL)_2ClO_4.2H_2O$	Powder	2.22		1.93

the extent of this temperature dependence will be

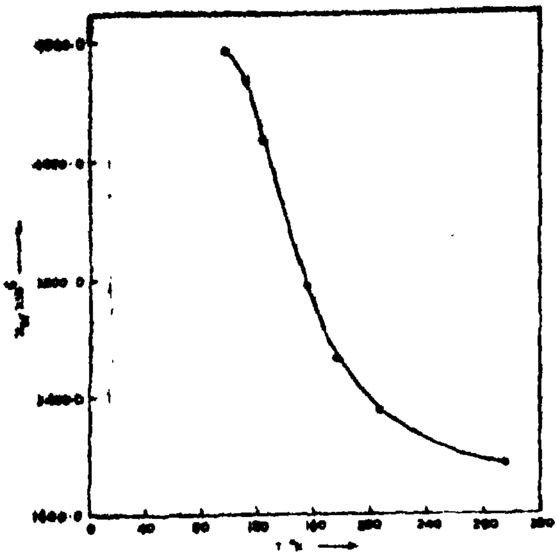


Fig. 1. Temperature Dependence of X_{M}, for Fe(III)—PAPL complex.

decided largely by the spiltting of the $^{2}T_{2g}$ in a ligand filed of low symmetry. Figgis *et al.*[9,10] have pointed towards limitations inherent in the above statement. The marked temperature independence of magnetic moment in Fe(III)-PAPL indicates the splitting of the tripl degenerate $^{2}T_{2g}$ ground term under the influenceyof obvious low symmetry of the ligand field. This view gets support from the ESR data dicussed below.

From the ESR spectra of the complexes, the 'g' values have been calculated following Kheubuhl[11] and presented in Table 3. EPR spectra of the low-spin iron (III) complexes with octahedral crystal filds of high symmetries, where the ground term is essentially $^{2}T_{2g}$, show two characteristic properties. The ESR signals are observed only at the very low temperature and the'g' values vary greatly from 2.0023. This is because three orbitals states of t_{2g}, close in energy, are connected by the spin orbital operator. The complexes under discussion on the other hand show ESR signals at room temperature and also the 'g' factors are not far from 2.0023. This suggests that the ground state is not essentially $^{2}T_{2g}$ and that some of its orbital degeneracy has been removed by the low symmetry component of the ligand field.

Acknowledgement

The authors are thankful to Dr. S. Mitra, Chemical Physics Group, Tata Institute For Fundamental Research, Bombay, to Prof. T. R. Govindachary, Director, CIBA-GEIGY Research Centre, Bombay and to Dr. B. S. Joshi, Scientist, Radiochemistry Division, BARC, Bombay for providing facilitie for low-temperature magnetic susceptibility measurements, microanalysis and ESR measurements, respectively. The work was carried out under the Financial Assistance to Teachers' scheme awarded to one of the authors by the University Grants Commission, New Delhi.

References

1. S. SHIBATA, in "Chelates in Analytical Chemistry" (N. A. Flaschka and A. J. Barnard Jr.) Vol. IV, Marcell Dekkar, Inc., N.Y., 1972.
2. V. CHISWELL, F. LIONS and M. L. TOMLINSON, *Inorg. Chem.*, 1964, 3, 492.
3. Y. K. BHOON, K. B. PANDEYA and R. P. SINGH, *Indian J. Chem.*, 1973, 13, 84.
4. Y. K. BHOON, K. B. PANDEYA and R. P. SINGH, *Indian J. Chem.* 1976, 14, (in press).
5. Y. K. BHOON, K. B. PANDEYA and R. P. SINGH *Indian J. Chem.*, 1976, 14, (in press).
6. B. N. FIGGIS and J. LEWIS in "Progr, in Inorg. Chem." Vol. 6 (F. A. Cotton, ed.), Interscience Publishers, N. Y., 1964.
7. B. CHISWELL and K. W. LEE, *Inorg. Chim. Acta*, 1972, 6, 567.
8. B. CHISWELL, *Inorg Chim. Acta*, 1975, 12, 195.
9. B. N. FIGGIS, *Trans. Faraday Soc.*, 1961, 57, 199.
10. B. N. FIGGIS, M. GERLOCH and R. MASON, *Proc. Roy. Soc.* A, 1969, 91, 309.
11. F. K. KHEUBUHL, *J. Chem. Phys.*, 1960, 33, 1074.

J. Indian Chem. Soc.,
Vol. LVII, March 1980 pp. 289-291

Potentiometric Studies on La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), Dy(III), Ho(III) and Y(III) Complexes of Tiron

B. C. BHUYAN and S. N. DUBEY*

Department of Chemistry, Kurukshetra University, Kurukshetra-132 119

Manuscript received 23 October 1979, accepted 30 December 1979

The formation constants of 1:1, 1:2 and 1:3 complexes of La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+} and Y^{3+} with Tiron have been studied potentiometrically in aqueous medium at different ionic strengths (0.05, 0.1, 0.15 and 0.2*M* KNO_3) and temperatures (25° and 35°) using Calvin-Bjerrum titration technique as modified by Irving and Rossotti. In general the stability sequence follows: $Ho^{3+} > Dy^{3+} > Y^{3+} > Tb^{3+} > Gd^{3+} > Sm^{3+} > Nd^{3+} > Pr^{3+} > Ce^{3+} > La^{3+}$. The thermodynamic stability constants, $\log K_1^{\mu=0}$ and $\log K_2^{\mu=0}$, have been determined by extrapolating the values to zero ionic strength. The thermodynamic functions (ΔG, ΔH and ΔS) accompanying complex formation have also been reported.

TIRON is a strong complexing agent and reported to form strong complexes with a number of metal ions[1-4]. From perusal of literature, it is evident that a systematic approach to the complexation reactions of lanthanides with tiron is lacking. The present paper reports the determination of the formation constants for lanthanide complexes at different ionic strengths and temperatures in aqueous medium using Calvin-Bjerrum *p*H-titration technique[5,6] as modified by Irving and Rossotti[7]. The thermodynamic stability constants and thermodynamic parameters are determined, and a graphical relationship between thermodynamic stability constants and inverse of ionic radii is depicted.

All the metal nitrate solutions (Rare Earths India Ltd.) were standardized by oxalate method[8]. The other chemicals were of B.D.H., A.R. grade. The solutions were made in doubly distilled water.

Results and Discussion

The proton-ligand stability constants of Tiron, $\log K_1^H$ and $\log K_2^H$, were found to be 12.53, 8.18 (μ=0.05 *M*, 25°); 12.36, 7.98 (μ=0.1 *M*, 25°); 12.23, 7.95 (μ=0.15 *M*, 25°); 12.19, 7.85 (μ=0.2 *M*, 25°) and 11.94 and 7.79 (μ=0.1 *M*, 35°), respectively. The formation constants, $\log K_1$, $\log K_2$ and $\log K_3$ were calculated using ligand and chelate titration curves and the values were further refined by different computational techniques[7,9]. The mean values are given in Table 1.

The general trend in overall stabilities ($\log \beta_3$ as well as $\log \beta_2$) of these complexes at 25° and 35° follows the order:

$$Ho^{3+} > Dy^{3+} > Y^{3+} > Tb^{3+} > Gd^{3+} > Sm^{3+} > Nd^{3+} > Pr^{3+} > Ce^{3+} > La^{3+}$$

However in case of Ce(III) it was not possible to determine $\log K_3$ value as $\bar{n}$ did not exceed 2.2. The decrease in stability ($\log K_1$ and $\log K_2$ values) with increase in ionic strengths and temperature indicates that lowering of the concentrations of indifferent electrolyte and temperature is favourable for complex formation. The thermodynamic stability constants ($\log K_1^{\mu=0}$ and $\log K_2^{\mu=0}$) have been evaluated at the standard state of infinite dilution. Thermodynamic stability constants ($\log \beta_2^{\mu=0}$) when plotted against inverse of ionic radii (Fig. 1) of the lanthanides showed a resonably increasing trend in the stabilities of these complexes with an irregularity near Gd^{3+} ion[10].

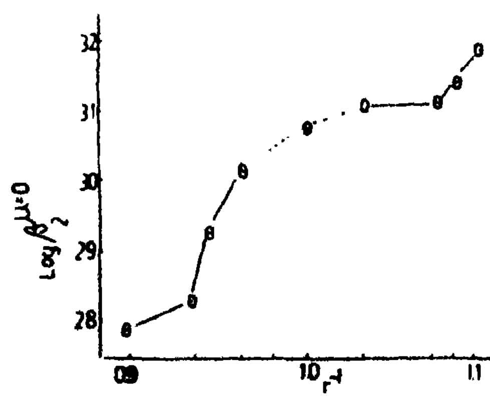


Fig. 1. Plot of Thermodynamic Stability Constants versus r^{-1} of Lanthanides.

*To whom correspondence is to be made

TABLE 1—STABILITY CONSTANTS OF TIRON COMPLEXES AT 25° AND 35°

Stability constants	La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Sm^{3+}	Gd^{3+}	Tb^{3+}	Dy^{3+}	Ho^{3+}	Y^{3+}
					$\mu = 0.05M$ (25°C)					
log K_1	13.82	14.36	14.76	14.96	15.14	15.26	15.34	15.40	15.57	15.07
log K_2	12.61	13.01	13.36	13.53	13.67	13.90	13.99	14.19	14.43	14.20
log β_2	26.43	27.37	28.12	28.49	28.81	29.16	29.33	29.59	30.00	29.27
log K_3	10.20	—	10.52	10.99	11.40	11.86	11.94	12.33	12.71	12.54
log β_3	36.63	—	38.64	39.48	40.21	41.02	41.27	41.92	42.71	41.81
					$\mu = 0.1M$ (25°C)					
log K_1	13.30	13.59	13.98	14.28	14.48	14.53	14.56	14.76	14.86	14.54
log K_2	12.24	12.54	12.85	13.01	13.20	13.51	13.65	13.79	14.11	13.80
log β_2	25.54	26.13	26.83	27.29	27.76	28.04	28.21	28.55	28.97	29.34
log K_3	9.72	—	10.13	10.39	10.64	11.26	11.69	11.97	12.50	11.95
log β_3	35.26	-	36.96	37.68	38.40	39.30	39.90	40.52	41.47	40.29
					$\mu = 0.15M$ (25°C)					
log K_1	13.12	13.50	13.67	14.01	14.22	14.24	14.29	14.48	14.65	14.31
log K_2	12.07	12.46	12.66	12.90	13.16	13.33	13.42	13.68	13.76	13.57
log β_2	25.19	25.96	26.33	26.91	27.38	27.57	27.71	28.16	28.41	27.88
log K_3	10.32	—	10.00	10.59	10.91	11.65	11.95	12.33	12.54	12.15
log β_3	35.51	—	36.33	37.50	38.29	39.22	39.66	40.49	40.95	40.03
					$\mu = 0.2M$ (25°C)					
log K_1	12.94	13.33	13.53	13.68	13.78	13.88	14.03	14.21	14.27	13.86
log K_2	11.91	12.27	12.53	12.75	12.85	13.07	13.38	13.49	13.63	13.37
log β_2	24.85	25.60	26.06	26.43	26.63	26.95	27.41	27.70	27.90	27.23
log K_3	9.98	-	10.38	10.55	10.80	11.45	11.89	12.38	12.53	12.10
log β_3	34.83	—	36.44	36.98	37.43	38.40	39.30	40.08	40.43	39.33
					$\mu = 0.1M$ (35°C)					
log K_1	13.25	13.42	13.76	13.91	14.08	14.24	14.27	14.58	14.82	14.49
log K_2	12.10	12.48	12.76	12.90	13.05	13.16	13.47	13.68	13.88	13.40
log β_2	25.35	25.90	26.52	26.81	27.13	27.40	27.74	28.26	28.70	27.89
log K_3	10.31	—	10.40	10.82	11.14	11.84	12.18	13.09	13.34	12.80
log β_3	35.66	—	36.92	37.63	38.27	39.24	39.92	41.35	42.04	40.69

The thermodynamic functions (ΔG, ΔH and ΔS) were calculated from the values of log β_2 and log β_3 at different temperatures using standard equations[11] and are given in Table 2. The overall changes in the values of ΔH and ΔS for log β_3 indicate that the complexes are both enthalpy and

TABLE 2—THERMODYNAMIC FUNCTIONS OF Ln^{3+}-TIRON COMPLEXES

Ln^{3+}	Free energy change K.cal. mole^{-1} (25°C)		Enthalpy change K.cal. mole^{-1} (25°C)		Entropy change Cal. mole^{-1} deg^{-1} (30°C)	
	$-\Delta G_2$	$-\Delta G_3$	$-\Delta H_2$	$-\Delta H_3$	ΔS_2	ΔS_3
La^{3+}	34.85	48.11	7.99	+16.82	88.59	214.15
Ce^{3+}	35.65	—	9.67	—	85.70	—
Pr^{3+}	36.61	50.43	13.03	1.68	77.75	160.79
Nd^{3+}	37.23	51.41	20.18	2.10	56.24	162.64
Sm^{3+}	37.87	52.39	26.49	5.47	37.56	154.79
Gd^{3+}	38.26	53.62	26.91	2.52	37.44	168.52
Tb^{3+}	38.45	54.43	19.76	+ 0.84	61.77	182.34
Dy^{3+}	38.95	55.28	12.19	+34.89	88.27	297.47
Ho^{3+}	39.53	56.58	11.35	+23.97	92.94	265.69
Y^{3+}	38.67	54.97	18.92	+16.82	65.14	236.80

entropy stabilized. Changes in enthalpy when plotted against inverse of ionic radii placed the lanthanides into two groups with Gd^{3+} as the dividing species[10] (Fig. 2).

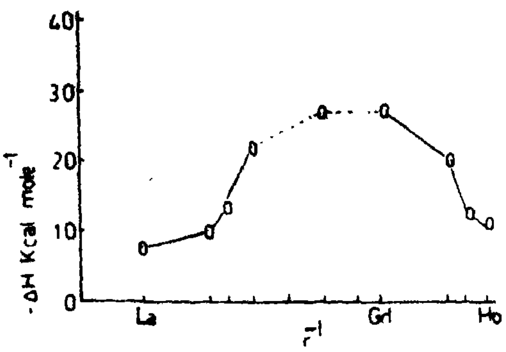


Fig. 2. Plot of changes in enthalpy($\triangle H$) versus r^{-1}.

The positive values of enthalpy (Table 2) suggest that the reactions in the third step are endothermic. A plausible explanation to this effect is that as the ionic size increases the incoming ligand experiences a short of repulsion from the groups already attached with the central ion. However entropy is favourable for complexation as large number of water molecules are set free from the highly hydrated lanthanide ions.

Acknowledgement

The authors thank Prof. H.L. Bhatnagar, Head of the Department of Chemistry, Kurukshetra University for providing necessary facilities and the U.G.C. for providing teacher-fellowship to one of them (BCB).

References

1. S. N. DUBEY and R. C. MEHROTRA, *J. Less Common Metals*, 1965, 9, 123.
2. S. N. DUBEY and R. C. MEHROTRA, *J. Indian Chem. Soc.*, 1965, 42, 685.
3. L. D. SHTENKE, N. A. OKORIK and V. N. KUMOK, *Zh. Neorg. Khim.*, 1970, 15, 1214.
4. SANTOSH D. MAKHIJANI and SATENDRA P. SANGAL, *Indian J. Chem.*, 1977, 15, 841.
5. M. CALVIN and K. W. WILSON, *J. Amer. Chem. Soc.*, 1945, 67, 2003.
6. J. BJERRUM, Metal amine formation in aqueous (P. Haase and Sons), 1941.
7. H. M. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.*, 1953, 3397 ; 1954, 2904.
8. G. B. WANGERT, R. C. WALKER and V. A. STENGER, *Analyst Chem.*, 1932, 24, 1936.
9. S. N. DUBEY and R. C. MEHROTRA, *Indian J. Chem.*, 1967, 5, 327.
10. T. MOELLER, The Chemistry of Lanthanides, Pergamon Press, 1973, 24, 30-32 and references therein.
11. K. B. YATSIMIRSKII and V. P. VASIL'EV, Instability constants of complex compounds, Pergamon Press, London, 1960, 59-65.

J. Indian Chem. Soc.,
Vol. LVII, March 1980, pp. 292-293

Analytical Applications of DEAPG as Gravimetric Reagent-I Estimation of Hg(II)

R. K. UPADHYAY and A. P. TEWARI*

Chemistry Department, N.R.E.C. College, Khurja (U.P.)

Manuscript received 12 October 1979, accepted 30 December 1979

p-Diethylaminoanil of phenyl glyoxal (abbreviated as DEAPG) precipitates Mercury(II) quantitatively and gives dark brown complex at pH 9.8 by adding double theoretical quantity of the ligand. It can be used for the gravimetric estimation of Hg(II) either alone or in presence of foreign ions.

A PERUSAL of literature on gravimetric analysis of metals reveals that many large organic compounds have been used in the inorganic quantitative estimations but ketoanils[1-3] have been rarely employed as precipitating reagents. Moreover gravimetric determination of Hg(II) was done by Nigam and Tewari[4] using 1-imino-3 thioisoindoline, Kaushik and Prasad[5] using Sodium meta periodate and Chaudhary and Das[6] using Cyclopentanone-2-carboxy anilide but no attempt has been made in the quantitative estimation of this ion by employing ketoanil (DEAPG) as precipitating agent so far. The present paper aims at using new ligand *p*-diethylaminoanil of phenylglyoxal for the gravimetric determination of Hg(II). The work incorporated in this paper describes the suitable conditions for the precipitation of metal ions by the ligand.

Experimental

Stock solution of metal chloride was prepared by dissolving pure compound in alcohol and was used after standardisation by standard methods[7]. Standard solution of ligand was prepared by dissolving its directly weighed quantity in the same medium. All the reagents and chemicals used were of either B.D.H. or E. Merck, A.R. and G.R. grades respectively. Ligand was prepared by method reported by Verma[8].

The *p*H of the solution was adjusted by using hydrochloric acid and sodium hydroxide. Phillips *p*H meter with glass and saturated calomel electrodes was used for *p*H measurements. G4-sintered glass crucibles (JENA) were used for gravimetric estimations.

In mercuric chloride solution, reagent was added very slowly with constant stirring till in slight excess. The quantitative reaction was ensured by adjusting *p*H with the solution of acid and alkali. Reaction mixture was left for four hours (preferably overnight) and was collected on sintered glass crucible. The precipitate was washed with ether several times to remove excess of reagent and was dried to constant weight.

Dark brown complex was soluble in acetone, acetonitrile and alcohol (after heating) while insoluble in benzene, carbontetrachloride, petroleum ether and ether. It was decomposed by conc. nitric and sulphuric Acids.

Results and Discussion

Effect of pH *Reagent Concentration and Temperature* :

In order to know the suitable conditions for the quantitative precipitation of Hg(II) with DEAPG, the precipitation of Hg(II)-DEAPG complex was carried out in the *p*H range from 7.8 to 12.0 by the addition of different quantity of the precipitant. After purification precipitates were dried and weighed from 50-130°. Data reported in Table 1 show that the weights of the precipitate found were almost corresponding to theoretical values of Hg(II)-DEAPG complex at 9.8 *p*H in the temperature range of 70-80° by adding double theoretical quantity of the ligand. Complex was found to be stable upto 140°.

Quantitative Gravimetric Estimation :

Under the above-mentioned conditions of *p*H, concentration of ligand and the temperature, gravimetric estimation of different quantities of Hg(II) were performed and results are noted in Table 2.

*Postal Address—A. P. Tewari, Chemistry Department, D. A. V. (P.G.) College, Bulandshahr-203 001, (U.P.).

TABLE 1—EFFECT OF pH, REAGENT CONCENTRATION AND TEMPERATURE

Observations at different pH (16.042mg Hg(II) ≡ 41.153mg Complex taken)		Observations at different Concentrations of reagent (16.042mg Hg(II) ≡ 41.153mg complex taken)		Observations at different temperatures (16.042mg Hg(II) ≡ 41.153mg complex taken)	
Weight of precipitate (mg)	pH	Weight of precipitate (mg)	reagent added (mg)	Weight of precipitate (mg)	Temperature °C
28.2	7.8	40.0	25.2	43.8	30
35.2	8.2	40.0	28.0	42 6	60
37.8	8.7	40.4	33.6	42.8	65
39.0	9.2	40.8	36.4	41.4	70
39.0	9.6	40.6	39.2	41.4	75
40.6	9.7	41.2	42.0	41.4	80
41.0	9.8	41.2	44.8	41.0	90
41.0	10.0	41.0	47.6	40.4	100
38.8	10.5	40.4	50.4	40.6	110
37.0	11.0	39.4	53.2	39.6	120
35.2	12.0	38.2	56.0	39.0	130

TABLE 2—GRAVIMETRIC DETERMINATION OF MERCURY WITH DEAPG

Hg taken (mg)	Weight of Complex (mg)	Hg found (mg)	Error (%)
10.02	25.6	9.98	−0.40
12.03	30.8	12.00	+0.24
16.04	41.2	16.06	+0.12
20.05	51.4	20.04	−0.05
24.06	61.8	24.09	+0.12
28.07	72.0	28.06	−0.03
32.08	82.4	32.12	+0.12
40.11	102.8	40.08	−0.07
48.13	123.4	48.10	−0.06
60.16	154.6	60.26	+0.16

Effect of Foreign Ions :

There was no interference by the addition of different quantities of following foreign ions on the precipitation of Hg(II) done in suitable conditions as are shown in Table 3.

TABLE 3—GRAVIMETRIC ESTIMATION OF MERCURY IN PRESENCE OF FOREIGN IONS

Hg taken (mg)	Foreign ion added (mg)		Weight of Hg Complex (mg)
16.042	F^-	(40)	41.6
16.042	Cl^-	(30)	41.6
16.042	Br^-	(20)	40.8
16.042	I^-	(30)	40.8
16.042	SO_4^{-2}	(25)	41.4
16.042	NO_3^-	(20)	40.8
16.042	Pd^{+2}	(30)	40.2
16.042	Au^{+3}	(25)	41.8

There are certain cations like Sn(II), Cd(II), Co(II), Cu(II), Zn(II), Ni(II) which interfered in the estimation of Hg(II).

Conclusion :

The analytical data indicate that DEAPG effectively be used as a gravimetric reagent for Hg(II). It is easy to filter and bring the precipitate to constant weight within a period of two hours or so. On account of high molecular weight of Hg(II)-DEAPG complex and low conversion factor for mercury makes the reagent (DEAPG) useful in the determination of micro quantities of metal. The precision and accuracy was found within the permissible limits.

In the light of above facts reagent DEAPG may be recommended as a promising gravimetric reagent for Mercury(II).

Acknowledgement

One of us (A.P.T.) is thankful to U.G.C., New Delhi for award of Teacher Fellowship and Dr. P. C. Gupta, Principal, N.R.E.C. College, Khurja for providing the laboratory facilities. We are also indebted to Dr. V.P. Singh for valuable suggestions.

References

1. R. K. UPADHYAY and R. C. SAXENA, *J. Indian Chem. Soc.*, 1973, **50**, 158.
2. R. K. UPADHYAY, V. P. SINGH, R. PRASAD and S. C. SHARMA, *J. Indian Chem. Soc.*, 1974, **51**, 528.
3. R. K. UPADHYAY, 'D. Sc. Thesis, Meerut Univ., Meerut India (1978).
4. A. K. NIGAM and G. D. TEWARI, *J. Indian Chem. Soc*, 1974, **51**, 912.
5. R. K. KAUSHIK and R. PRASAD, *J. Indian Chem. Soc.*, 1973, **50**, 17.
6. N. K. CHAUDHARY and J. DAS, *J. Indian Chem. Soc.*, 1976, **53**, 33.
7. A. I. VOGEL, "A Text Book of Quantitative Inorganic Analysis", Longman Group Ltd., London (1969).
8. H. P. S. VERMA, 'Ph. D. Thesis', Meerut Univ., Meerut, India (1975).

J. Indian Chem. Soc.,
Vol. LVII, March 1980, pp. 294-296

Paper Chromatographic Studies of Some Cations with Solvents Containing N, N-Dimethylformamide (DMF)†

K. D. SHARMA and (Miss) NEELAM RATTAN

Department of Chemistry, Maharaja College, Chhatarpur (M.P.)

Manuscript received 10 October 1979, accepted 30 December 1979

N, N-Dimethylformamide (DMF) and mixtures containing DMF with many non-aqueous solvents have been tested as possible solvent systems for the separation of Pb^{++}, Ag^{+}, Hg^{++} and Tl^{++} ions on discs and strips of Whatman No. 1 and 3 mm chromatographic papers. Rf values for these ions have been reported in about 56 solvent systems which include pure, binary and ternary mixtures each containing DMF. Separation of different combinations of these ions have been achieved successfully in some of these mixed solvent systems.

REGARDING the suitability of a solvent system, no theoretical predictions can be made strictly. But from the perusal of the literature it is seen that in the field of inorganic paper chromatography, the solvents generally used so far are either those with high polarity such as alcohols, ketones, ethers and esters ; or those which possess complex forming tendency such as acetylacetone, acetoacetic ester etc. Besides these, few recent papers describe the systematic investigation of less polar solvents like chloroform[1-3] for the inorganic paper chromatography and emphasize the utility of mixed systems.

N,N-Dimethylformamide is one such solvent, which incorporates both the above properties in it i.e., high polarity (dielectric constant = 36.7 at 25°) and tendency to form complexes[4,4-6] with metallic ions. Therefore it is expected to prove a good fundamental solvent for the paper chromatography of inorganics.

So far this solvent has been used mostly as stationary phase in the chromatography of organic compounds by few workers[5,6]; Baeyer *et al.*[7] have used DMF, mixed with *n*-butanol and water (1:9:10) as mobile phase for the separation of aliphatic aldehydes. This has also been used in TLC of organic compounds[8-10]. The use of DMF as mobile phase for inorganic paper chromatography has been virtually neglected and hence needs systematic investigation. The present studies therefore have been carried out with the view of using DMF (pure and mixed) for paper chromatography of the cations of the first group of analytical chart i.e. Pb^{++}, Ag^{+}, Hg^{++} and Tl^{+} which have been separated previously by Bhatnagar and Sharma[3] in mixed solvents containing chloroform.

Experimental

(a) *Apparatus, Paper and Reagents :*

For the radial development of the chromatogram, circular chromatographic troughs (20x20x50 cm) and for ascending and descending developments, cylindrical gas jars (12 cm diam. x 35 cm height) with usual accessories were used. Whatman No. 1 filter paper was used throughout for Rf measurements, and separations were done on No. 1 as well as 2 mm chromatographic paper.

Solutions of Lead(II), Silver(I), Mercury(II) and Thallium(I) ions were prepared from their nitrates (E.Merck & Proanalysi quality). The concentrations of cations for Rf measurements were 5 to 10 μg per 100 ml and for separation purpose 20 μg per 100 ml.

DMF was distilled under reduced pressure[4] and all other solvents were double distilled. All the mixed solvents, each containing DMF were prepared on volume to volume basis except in case of phenol where it was on weight to volume basis. Glacial acetic acid (BDH) was used as such to acidify the solvent system on volume to volume basis. Yellow ammonium sulphide solution was used as spray-reagent to locate the spots.

(b) *Procedure :*

Rf values of cations were determined on Whatman No. 1 discs (11 cm diameter) by usual Rutter's technique of radial development with the slight modification in spotting the solution. The wick was cut out from the centre tapering towards peripheri. The ions were spotted equidistant on a circle around the connecting end of the wick and the chromatogram was obtained as usual. The Rf values were then measured with respect to outer and inner fronts and reported as Rf (o) and Rf (i).

The separations of suitable combinations of the cations were carried out where differences in Rf values permitted to do so. For separations, the mixture of cation solution was spotted at the centre

† This paper was presented at the 'Convention of Chemists' 1978, Waltair (Andhra Pradesh), India.

of the disc which gave concentric rings for the different cations. The separations were also carried out on the strips.

Results and Discussion

Rf values for cations under study have been summarised in Table 1 (as Rf (o) x 100 and Rf (i) x 100). The solvents have been denoted by English alphabet as A=DMF, B=chloroform, C=Carbon tetrachloride, D=Phenol, E=*n*-butanol, F=isopropanol, G=acetone, H-methyl ethyl ketone, I=methyl acetate, J=acetic acid (Glacial) and K=nitric acid (16 *N*).

From the study of Rf values it is clear that most of the ions do not migrate in less polar or non-polar pure solvents like-chloroform[11] isopropanol and carbontetrachloride. In pure DMF, all the ions move upto sufficient distances. Lederer[12], Pollard

TABLE 1—RF VALUES OF CATIONS X 100

S. No.	Solvent System	Composition	Ag^+ Rf(o)-Rf(i)	Pb^{++} (o)-(i)	Hg^{++} (o)-(i)	Tl^+ (o)-(i)
1.	A	Pure	50-32	72-50	99-86	60-42
2.	B	Pure	d	d	d	d
3.	A:B	1:1	22-d	75-69	100-83	52-d
4.	A:B	1:2	24-d	76-69	92-76	56-d
5.	A:B	1:3	22-d	78-72	97-88	63-43
6.	A:B:J	1:1:2%	00-00	78-82	100-74	66-41
7.	A:B:J	1:2:2%	00-00	93-73	97-83	50-d
8.	A:B:J	1::32%	00-00	45-31	92-83	33-17
9.	C	Pure	d	d	d	d
10.	A:C	1:1	41-d	63-d	93-81	61-d
11.	A:C	1:2	45-d	78-62	96-76	47-d
12.	A:C	1:3	68-50	80-68	100-72	65-45
13.	A:C:J	1:1:2%	60-41	69-T	100-90	68-31
14.	A:C:J	1:2:2%	52-d	72-34	96-64	43-d
15.	A:C:J	1:3:2%	62-41	85-70	100-79	60-32
16.	A:D	5%(w/v)	56-37	75-68	100-57	50-25
17.	A:D	10%(w/v)	46-d	62-55	100-84	48-d
18.	A:D	15%(w/v)	36-d	62-44	84-44	27-d
19.	A:D:J	5%:2%	45-d	67-60	84-85	41-d
20.	A:D:J	10%:2%	56-d	93-90	100-86	50-37
21.	A:D:J	15%:2%	50-d	93-89	100-83	55-44
22.	E	Pure	00-00	83-61 T	91-82	65-20
23.	A:E	1:1	28-d	73-44	100-93	37-d
24.	A:E	1:2	00-00	46-d	93-83	26-15
25.	A:E	1:3	00-00	64-47	100-95	93-68
26.	A:E:J	1:1:2%	00-00	57-42	100-94	46-d
27.	A:E:J	.1:2:2%	11-d	44-34	97-90	19-13
28.	A:E:J	1:3:2%	00-00	63-25	100-93	79-62
29.	F	Pure	00-00	d	100-95 T	00-00
30.	A:F	1:1	00-00	d	100-91	21-d
31.	A:F	1:2	00-00	40-d	90-80	24-d
32.	A:F	1:3	00-00	69 52	100-87	50-d
33.	A:F:J	1:1:2%	00-00	56-d	97-91	29-d
34.	A:F:J	1J2:2%	00-00	39-d	88-79	13-d
35.	A:F:J	1:3:2%	00-00	81-78 M	100-80	37-d
36.	G	Pure	73-d	40-d	100-78	60-13
37.	A:G	1:1	50-d	83-75	92-78	50-d
38.	A:G	1:2	50-d	74-71	94-73	52-d
39.	A:G	1:3	34-d	79-71	100-81	52-24
40.	A:G:J	1:1:2%	55-d	74-44	100-94	50-25
41.	A:G:J	1:2:2%	62 41	76-69	100-78	50-14
42.	A:G:J	1:3:2%	64-48	88-76	100-85	63-17
43.	H	Pure	78-d	76-69	100-86	87-66
44.	A:H	1:1	52-d	83-75	100-86	52-43
45.	A:H	1:2	44-38 M	41-37	84-72	37-d
46.	A:H	1:3	36-d	76-60	94-76	48-12
47.	A:H:J	1:1:2%	58-45	83-79	100-76	47-d
48.	A:H:J	1:2:2%	70-40	79-76	100-85	50-d
49.	A:H:J	1:3:2%	64-45	84-74	100-78	60-30
50.	A:I	1:1	64-40	50-30	31-08	69-19
51.	A:I	1:2	74-35	80-67	80-60	76-64
52.	A:I	1:3	96-75	93-74	87-69	92-71
53.	A:I:J	1:1:2%	96-76	85-70	82-68	85-63
54.	A:I:J	1:2:2%	93-78	87-73	84-68	100-73
55.	A:I:J	1:3:2%	91-74	90-71	85-65	72-76
56.	A:E:K	3:1:2%	64-50	87-81	100-86	36-07

d = diffusion, T = tailing, M = multiple spotting.

et al.[13] and Haraswa[14] have shown the need of solvents either with high but different polarity (usually highly polar solvents) or with complexing property, for effective separation of inorganic ions. DMF possesses both these characteristics in it i.e. high polarity and complex forming property. The results of present study indicate that the high Rf values in pure DMF may be due to its high polarity. In mixed solvents some regularities have been observed. The Rf values in mixed solvents increase in general with the increasing ratio of chlofororm, carbontetrachloride and isopropanol which is not in accordance with the expectations and previous findings[11]. Hence it may be concluded that in mixed systems polarity alone may not be the only factor effecting migration. The deviation in values from expected should be due to the solvating effect of the solvent on the adduct[4] formed between metal ion and DMF. The decreasing Rf values with increasing concentration of phenol in DMF are in the order of decreasing basic character of the system. Systems containing *n*-butanol have been largely employed successfully in chromatography. In the present study also it proved a good system with DMF. Presence of mineral acid gives still better results and compact rings in this system as tested for one system No. 56 (Table 1) only.

Separations achieved in different combinations of cations are tabulated in Table 2. Binary separations are possible many in number and have not been mentioned; only ternary and quaternary separations are tabulated. Separations of cations in solvents without acid (proton) conform to the mechanism as proposed by Bhatnagar and Bhatnagar[15] on impregnated papers.

TABLE 2—SEPARATIONS ACHIEVED

S.No.	Ions separated	Solvent system No.
1.	Ag^{+}, Tl^{+}, Hg^{++}	24
2.	Ag^{+}, Pb^{++}, Hg^{++}	25
3.	Pb^{++}, Hg^{++}, Tl^{+}	27
4.	Ag^{+}, Pb^{++}, Hg^{++}, Tl^{+}	28
5.	Ag^{+}, Pb^{++}, Hg^{++}, Tl^{+}	6
6.	All the four ions	31
7.	All the four ions	46
8.	All the four ions	49

Time of run of the chromatogram ranges from 3 to 3.30 Hours at 32-34°.

References

1. R. P. BHATNAGAR and N. S. POONIA, *Anal. Chem.*, 1962, 34, 1325.
2. R. P. BHATNAGAR and K. D. SHARMA, *Anal. Chim. Acta*, 1964, 30, 310.
3. R. P. BHATNAGAR and K. D. SHARMA, *Indian J. Appl. Chem.*, 1966, 29, 133.
4. R. G. MISHRA, Ph.D. Thesis, A. P. S. University, Rewa 1976.

4.a R. C. PAUL, S. SARDA and B. P. SREENATHAN, *Indian J. Chem.*, 1964, 2, 97.

5. L. HORNER and W. KIRMSE, *Ann. Chem.*, 1955, 48, 597.
6. S. HUDECEK, *Chem. Listy*, 1955, 60, 49.
7. E. BAEYER, K. H. REUTTER and R. TERHEID, *Chem. Ber.*, 1961, 90, 1929.
8. K. W. GLOMBITZKA, *J. Chromatog* (in press).
9. D. ARZNEIMITTEL, NORDAN, *Froseh*, 1964, 14, 1354.
10. R. KLEMENT and A. WILD, *Z. Analyst. Chem.*, 1963, 195, 180.
11. K. D. SHARMA, Ph.D. Thesis, Jiwaji University, Gwalior (1967).
12. M. LEDERER, *Anal. Chim. Acta*, 1950, 4, 629.
13. I. I. M. ELBEIH, J. F. W. MCOMIE and F. H. POLLARD, *Discuss. Faraday Soc.*, 1949, 7, 183.
14. S. HARASWA, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1951, 72, 107, 236, 423.
15. R. P. BHATNAGAR and N. P. BHATNAGAR *Indian J Chem.*, 1977, 17 A, 1089.

J. Indian Chem. Soc.,
Vol. LVII, March 1980, pp. 297-299

Potentiometric Studies on Stepwise Mixed Ligand Chelate Formation of La(III), Pr(III) or Nd(III)-N-Hydroxy Ethylethylenediamine-N, N′, N′-Triacetic Acid-Mercapto Acids

H. S. RANA* and J. P. TANDON

Chemical Laboratories, University of Rajasthan, Jaipur

Manuscript received 19 April 1979, accepted 25 December 1979

Sloution equilibrium studies on the interaction between 1 : 1, Ln(III)-HEDTA binary chelate (where Ln(III) = La(III), Pr(III) or Nd(III) ; HEDTA = N-hydroxyl-ethylethylenediamine-N,N′, N′-triacetic acid) with certain mercapto acids such as thioglycollic (TGA) and thiomalic (TMEA) have been carried out potentiometrically. Formation constants of the resulting mixed ligand chelates, MAL (where M = La(III), Pr(III) or Nd(III) ; A = HEDTA and L = TGA or TMEA) have been determined at 30±1° and μ = 0.1 (KNO_3). The values of the formation constant K_{MAL} have been interpreted in terms of electrostatic repulsion indicating that the contribution due to π-interaction in M-S bond is not significant. The order of stability in terms of metal ions has been found to be La(III) < Pr(III) < Nd(III) and in terms of secondary ligand as TGA < TMEA.

N-hydroxyethylethylenediamine-N, N′, N′-triacetic acid is known to form quite stable complexes with a number of metal ions[1-4] and behaves as a pentadentate ligand[4]. In case the coordination number of the metal ion is not satisfied during the formation of binary complex (MA), the remaining sites are occupied by the water molecules or hydroxide ions[5,6]. However, in presence of a bidentate ligand these may be replaced resulting in the mixed ligand chelate (MAL) formation. Mercapto acids are known to interact with metal ions at higher pH[7-11] and the systems are interesting due to the presence of M-S bond[12]. In the present communication an attempt has been made to investigate the systems MAL, where M = La(III), Pr(III) or Nd(III) ; A = HEDTA and L = TGA or TMEA, in order to observe the contributions of π interaction in the M-S bond.

Experimental

The rare-earth oxides were of spectral grade and a stock solution was prepared and standardised as described in earlier communication[13]. The dipotassium salt of HEDTA (Koch Light, England) was prepared by dissolving its known amount in the required volume of KOH (0.1 *M*). The solutions of thioglycolic (E. Merck) and thiomalic (E. Merck) acids were prepared by direct weighing and standardized potentiometrically. All the solutions were prepared in doubly distilled water and the following *p*H-metric titrations were carried out at 30±1° using a Cambridge *p*H-meter standardized against 0.05 *M* potassium hydrogen phthalate solution.

1. 10ml (0.025 *M*) mercapto acid.
2. 10ml (0.025 *M*) dipotassium salt of HEDTA in presence of 10ml (0.025 *M*) Ln-nitrate (Ln(III)-HEDTA, 1 : 1).
3. 10ml (0.025 *M*) dipotassium salt of HEDTA in presence of 10ml (0.025 *M*) Ln-nitrate and 10ml (0.025 *M*) mercapto acid (Ln(III)-HEDTA-Mercapto acid, 1 : 1 : 1).

The ionic strength of all the solutions was kept constant (μ=0.1) by adding 5ml of 1*M* potassium nitrate and the total volume was raised to 50 ml in each case. The titrations were carried out in presence of an inert atmosphere.

Results and Discussion

Curves a and a′ (Figs.1 to 3) represent the potentiometric titrations of thioglycollic and thiomalic acids respectively. The acid dissociation constants (k_1, k_2 or k_3) of these ligands were calculated by algebraic method described by Chaberek and Martell[14]. The values of pk_1 and pk_2 in case of thiomalic acid were taken from the literature[15] and presented in Table 1.

TABLE 1—ACID DISSOCIATION CONSTANTS OF LIGANDS AT 30±1°C

Ligand	pk_1	pk_2	pk_3
Thioglycollic acid	3.61	10.28	
Thiomalic acid	3.64	4.64	10.32

*For correspondence—Department of Chemistry, N. R. E. C. College, Khurja-203 131.

TABLE 2—FORMATION CONSTANTS OF MIXED LIGAND CHELATES

$\mu = 0.1$; $t = 30 \pm 1°C$

L	$\text{Log } K^{La.HEDTA}_{La.HEDTA.L}$	$\text{Log } K^{Pr.HEDTA}_{Pr.HEDTA.L}$	$\text{Log } K^{Nd.HEDTA}_{Nd.HEDTA.L}$
TGA	3.18±0.08	3.55±0.09	3.77±0.08
TMBA	3.67±0.05	3.94±0.06	4.22±0.07

Curve b, (Figs. 1 to 3) may be attributed to the titration of 1 : 1 binary mixtures of Ln(III)-HEDTA, which exhibits an inflexion at m=1 (m=moles of base added per mole of metal ion). The inflexion at m=1, may be correlated to the formation of 1 : 1 M(III)-HEDTA binary chelates due to the neutralization of the free proton of the carboxylic group of HEDTA. The superimposable nature of the theoretical composite curve[16] in the lower buffer region supports the stepwise formation of the mixed ligand chelates in each case and the interaction of thio acid starts just after the complete formation of 1 : 1, M(III)-HEDTA binary complex. The initial lowering of *p*H in the case of 1:1:1 ternary systems (curves d and d', Figs. 1 to 3) may be due to the ionization of the proton of the carboxylic groups of mercapto acids. The formation constants K_{MAL} of the resulting mixed ligand chelates have been calculated (1) and listed in Table 2.

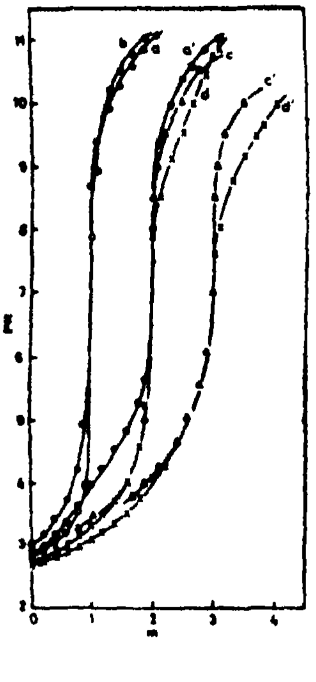


Fig. 1. Potentiometric Titrations of La(III)-HEDTA-TGA ; TMEA Ternary systems, (a) TGA ; (a') TMBA ; (b) 1:1, La(III)-HEDTA ; (d) 1:1:1 La(III)-HEDTA-TGA ; (d') 1:1:1 La(III)-HEDTA-TMEA ; (c, c') corresponding composite curves of mixed systems. m = moles of base added per mole of metal ion.

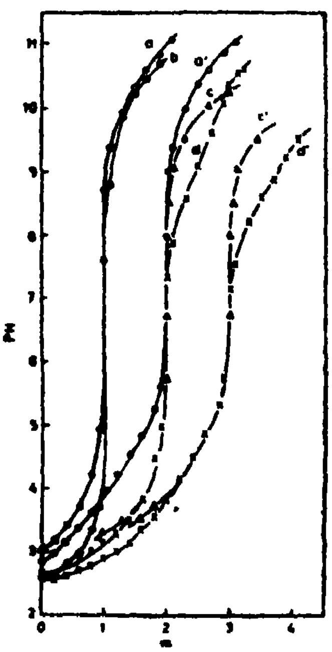


Fig. 2. Potentiometric Titrations of Pr(III)-HEDTA-TGA ; TMEA Ternary systems. (a) TGA ; (a') TMEA ; (b) 1:1, Pr(III)-HEDTA ; (d) 1:1:1 Pr(III)-HEDTA-TGA ; (d') 1:1:1 Pr(III)-HEDTA-TMEA ; (c, c') corresponding composite curves of mixed systems. m = moles of base added per mole of metal ion.

Systems : Ln(III)-HEDTA-TGA

Curve d (Figs. 1 to 3) corresponds to the potentiometric titration of 1 : 1 : 1 Ln(III)-HEDTA-TGA ternary systems and a sharp inflexion at m=2, may be correlated to the neutralization of the carboxylic proton in mercapto acid prior to its interaction with the 1 : 1, Ln(III)-HEDTA simple chelate. After m=2, a lower buffer region starts clearly showing the formation of the mixed ligand chelate (MAL) between m=2 to m=3 and this can be further substantiated by comparing the curve d (Figs. 1 to 3) with the corresponding composite curve c.

Systems : Ln(III)-HEDTA-TMEA

The equimolar systems, Ln(III)-HEDTA-TMEA (curve d', Figs. 1 to 3) on titration give a sharp inflexion at m = 3, which indicates that the neutralization of the carboxylic protons in the thiomalic acid takes palce prior to its interaction with 1 : 1, Ln(III)-HEDTA binary complex. The lowering of the buffer region after m=3 indicates the formation of 1 : 1 : 1 mixed species. The existence of such species between m=3 to 4 may be further substantiated by comparing the curve d' (Figs. 1 to 3) with the corresponding composite curve c'.

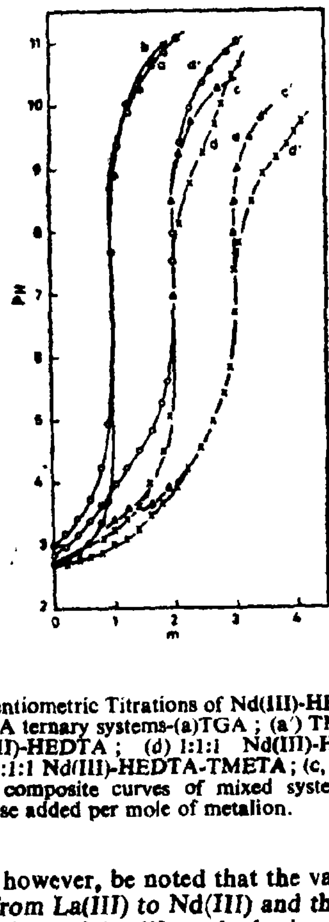


Fig. 3. Potentiometric Titrations of Nd(III)-HEDTA- TGA, TMEA ternary systems-(a)TGA ; (a') TMEA ; (b) 1:1, Nd(III)-HEDTA ; (d) 1:1:1 Nd(III)-HEDTA-TGA, (d') 1:1:1 Nd(III)-HEDTA-TMETA ; (c, c') corresponding composite curves of mixed systems m=moles of base added per mole of metalion.

It may however, be noted that the value of K^{MA}_{MAL} increases from La(III) to Nd(III) and this trend can reasonably be explained[17] on the basis of the increasing complexing power of the rare earth ions as the atomic number increases.

The value of K_{MAL} has been found to be lower than K_{MA}[4] in each case. It may be due to the absence of electrostatic attraction between the incoming charged hydroxy acid ion and the neutral 1 : 1, Ln(III)-HEDTA simple chelate, basicity of the incoming ligand and steric interference of HEDTA which occupies more space around the metal ion.

The stability of $K^{M.HEDTA}_{M.HEDTA.L}$ (where L'=Glycolic (GA) or malic acid (MEA) has been reported[18] and found to be greater than $K^{M.HEDTA}_{M.HEDTA.L}$ (where L= TGA or TMEA). This may be explained on the basis of the fact that rare-earth ion behaves as a class 'A' acceptor for which oxygen is a better donor atom. It is, therefore, concluded that M-Sπ-interaction, even if present, has no significant contribution to the stability in these cases.

In terms of the secondary ligands the formation constants of the resulting biligand complexes of any particular rare-earth ion increase in the following order:

TGA<TMEA

The greater stability of the thiomalic acid complexes may be due to the increase in the number of chelate rings formed and the basicity of the ligand involved.

Acknowledgement

Our thanks are due to Prof. K. C. Joshi for providing the necessary Laboratory facilities. The financial assistance from U.G.C. to one of us (H.S.R.) is thankfully acknowledged.

References

1. L. C. Thompson and J. A. Lorass, *Inorg. Chem.*, 1963, **2**, 89.
2. U. Yucelik Ozer, *J. Inorg. Nuclear Chem.*, 1970, **32**, 1279.
3. G. H. Carey, R. F. Bogucki and A. E. Martell, *Inorg. Chem.*, 1964, **3**, 1288.
4. T. Moeller and R. Ferrus, *J. Inorg. Nuclear Chem.*, 1961, **20**, 261.
5. N. D. Mitrofanova and L. I. Martynenko, *Russ. J. Inorg. Chem.*, 1962, **7**, 539.
6. G. Schwarzenbach and R. Gut, *Helv. Chim. Acta*, 1956, **39**, 1589.
7. D. I. Leussing, *J. Amer. Chem. Soc.*, 1958, **80**, 4180.
8. Q. Fernando and H. Freiser, *J. Amer. Chem. Soc.*, 1958, **80**, 4928.
9. D. D. Perrin and I. G. Sayce, *J. Chem. Soc.*, 1967, **82**.
10. R. S. Saxena, K. C. Gupta and M. L. Mittal, *Canad. J. Chem.*, 1968, **46**, 311.
11. D. D. Perrin and L. J. Porter, *Aust. J. Chem.*, 1969, **22**, 267.
12. S. Ahrland, J. Chatt and N. R. Davies, *Q. Rev. Chem. Soc.*, 1958, **12**, 265.
13. H. S. Rana and J. P. Tandon, *Moh. fur. Chemie*, 1975, **106**, 559.
14. S. Chaberek and A. E. Martell, *J. Amer. Chem. Soc.*, 1952, **74**, 5052.
15. G. R. Lenz and A. E. Martell, *Inorg. Chem.*, 1965, **4**, 378.
16. G. H. Carey and A. E. Martell, *J. Amer. Chem. Soc.*, 1967, **89**, 2859.
17. T. Moeller, D. E. Martin, L. C. Thompson, R. Ferrus, G. R. Feistel and W. I. Randall, *Chem. Revs.*, 1965, **65**, 1.
18. H. S. Rana and J. P. Tandon, *Zhurnal Obshchei Khimii*, 1978, XLVIII, No. 9, 1932.

J. Indian Chem. Soc.,
Vol. LVII, March 1980, pp. 300-303

Spectral and Magnetic Studies of Manganese(II) Complexes

D. S. SANKHLA and SUDHINDRA N. MISRA

Department of Chemistry, University of Jodhpur, Jodhpur-342 001, India

Manuscript received 12 October 1979, accepted 30 December 1979

Synthetic and characterization studies of diaqua manganese(II)-tetra thiourea dichloride complex $[Mn(tu)_4(H_2O)_2]Cl_2$, and its mixed ligand complexes with various nitrogen donor ligands are reported. These complexes have been characterized by magnetic, diffuse reflectance and infrared spectral studies apart from the elemental analyses. The diffuse reflectance spectra were performed and values of Racah inter-electronic repulsion parameter B and C, Slater-Condon-Shortly parameter F_2 and F_4, crystal field splitting energy (Dq), nephelauxetic ratio (β) and nephelauxetic parameter for coordinated ligand (h_x) have been calculated. From infrared studies it has been possible to assign whether the thiourea molecules present in complexes are coordinated to the metal ion through sulfur or nitrogen atom.

MANGANESE(II) ion has d^5 configuration and is capable of forming spin-free as well as spin-paired complexes. Due to the additional stability of the half filled d-shell, the spin-free complexes are most predominent. The equilibrium constant for their formation in aqueous solution are not high as compared to those for bivalent cations of succeeding element (Fe^{2+}-Cu^{2+}), because of manganese(II) is the largest of these and it has no ligand field stabilization energy in its complexes[1]. Manganese(II) complexes are susceptible to oxidation[2,3], but the complexes synthesized in the present study have been found to be sufficiently stable and resist oxidation. In these ligand exchange reactions, the comparatively weak bonded water molecules of parent diaqua-tetrathiourea manganese(II) dichloride complex $[Mn(tu)_4(H_2O)_2]Cl_2$, are quantitatively replaced by nitrogen donor ligand or ligands. The spectra in the solution however, could not be obtained because of the weak intensity of the bands and lack of the high solubility of these complexes in organic solvents and hence diffuse reflectance spectra have been carried out.

Experimental

Preparation of diaqua tetrathiourea manganese(II) dichloride complex, $(Mn(tu)_4(H_2O)_2]Cl_2$:

Manganese(II) chloride tetrahydrate (19.78 gm ; 0.1 mol) and thiourea (30.44 gm : 0.4 mol) were added to ethanol (300 ml). About 10 ml of water was then added to increase the solubility of the reactants. The reaction mixture was refluxed for three hours, on cooling the crystals of complex were separated. The crystals were filtered, washed with small portions of ethanol and dried under vacuum. Yield = 41 gm ; 80%. Melting point 131°. Elemental analyses data are given in the Table 1.

Preparation of mixed ligand complexes :

To a hot solution of diaqua tetrathiourea manganese(II) dichloride complex (0.01 mol) in dry ethanol (60 ml) was added an ethanolic solution of the ligand viz. pyridine or aniline or quinoline (0.02 mol), or 1,10-phenanthroline or 2,2'-bipyridine or

TABLE 1—ANALYTICAL DATA, MELTING POINT AND MAGNETIC MOMENT

Complex	% Metal		% Nitrogen		% Sulfur		M.P. in °C	μ_{eff} (in B.M.)
	Reqd.	Found	Reqd.	Found	Reqd.	Found		
$[Mn(tu)_4(H_2O)_2]Cl_2$	11.78	11.8	24.03	24.1	27.50	27.4	131	5.98
$[Mn(tu)_4(py)_2]Cl_2$	9.33	9.2	23.80	23.7	21.79	21.8	144	5.95
$[Mn(tu)_4(phen)]Cl_2$	8.99	9.0	22.94	22.9	21.00	20.9	350*	6.12
$[Mn(tu)_4(bipy)]Cl_2$	9.36	9.3	23.88	23.9	21.86	21.9	350*	6.14
$[Mn(tu)_4(qu)_2]Cl_2$	7.95	7.9	20-29	20.2	18.58	18.5	83	6.21
$[Mn(tu)_4(ani)_2]Cl_2$	8.91	8.8	22 72	22.7	20.81	20.7	110	6.00
$[Mn(tu)_4(en)]Cl_2$	11.20	11.2	28.56	28.5	26.15	26.1	102	6.16

tu=Thiourea ; py=Pyridine ; phen=1,10-Phenanthroline ; bipy=2,2'-Bipyridine ; qu=quinoline ; ani=Aniline ; en=Ethylenediamine ; μ_{eff}=Magnetic moment ; *=Do not melt.

ethylenediamine (0.01 mol). On cooling, the complex separated out from the solution. It was filtered washed with ether and dried in vacuum over anhydrous calcium chloride. Purity of these complexes was checked by elemental analyses (Table 1) manganese(II) was estimated[4] as $MnNH_4PO_4H_2O$.

Physical Measurements :

Magnetic measurements were carried out on Gouy magnetic balance at 300 ± 1^0K. Diffuse reflectance spectra in the UV and visible region were recorded on a VEB Carl Zeiss Jena VSU-2 Spectrophotometer using an annular ring type attachment o/r. The infrared spectra of these complexes have been recorded on a Perkin-Elmer 577 Spectrophotometer in KBr pallet in the region 000-400 cm^{-1}.

Results and Discussion

Manganese(II) complexes are generally spin-free complexes. Since spin-free manganese(II) complexes have an orbitally non-degenerate ^6s ground term, spin-only magnetic moment of 5.92 B.M. is expected which will be independent of the temperature and the stereochemistry[5,6]. In present course of study the complexes show magnetic moment value in the range 5.95-6.21 B. M. (Table 1) suggesting thereby that these are spin-free complexes having five unpaired electrons.

The electronic spectra of manganese(II) complexes show that bands are weak in intensity and number of bands is quite large. In Mn(II) complexes the intensity of the electronic transitions from the ground state ^6s to the states of four fold multiplicity are very weak and since Mn(II) has a d five electronic configuration the same type of energy-level diagram applies whether the metal ion is surrounded by tetrahedral or octahedral environment. In hexaaqua manganese(II), six electronic bands in two groups of three have been observed[1]. Only four bands could be observed in the diffuse reflectance spectra of manganese(II) complexes studied in the present work. These four observed bands representing corresponding transitions and energy in terms of Racah parameter[7] are viz. $^6A_{1g} \rightarrow ^4T_{1g}$ (^4G), (10B+5C), $^6A_{1g} \rightarrow ^4E_g$, $^4A_{1g}$ (^4G), (10B+5C), $^6A_{1g} \rightarrow ^4E_g$ (^4D), (17B+5C) and $^6A_{1g} \rightarrow ^4T_{1g}$ (^4P), (7B+7C). Diffuse reflectance spectra for some complexes have been plotted in remission function vs wave length (Fig. 1). Kubelka-Munk remission function $F=(1-R)^2/2R$, was used as a measure of absorption by powdered sample, where R is the diffuse reflectance. The electronic spectral pattern of all the complexes has been found to be similar.

The experimentally observed transition energies and calculated values for parameters B, C, Dq and β are summarized in the Table 2. The values obtained for the parameters B and C by using the transitions $^6A_{1g} \rightarrow ^4T_{1g}$ (^4G) and $^6A_{1g} \rightarrow ^4T_{1g}$ (^4P) are negative which have no physical significance, while

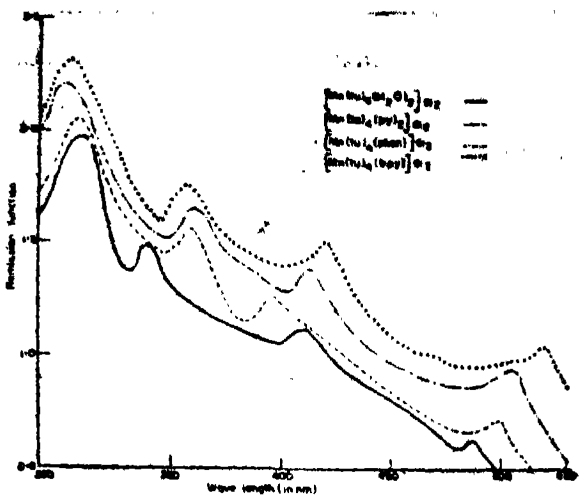


Fig. 1.

the transitions $^6A_{1g} \rightarrow ^4E_g$, $^4A_{1g}$ (^4G) and $^6A_{1g} \rightarrow ^4T_{1g}$ (^4P) yield the absurd values for parameter B and hence values are not included in the table. The best set of values for parameter B and C could be obtained using transitions $^6A_{1g} \rightarrow ^4E_g$, $^4A_{1g}$ (^4G) and $^6A_{1g} \rightarrow ^4E_g$ (^4D), this is due to the fact that the energies of these two transitions are independent on crystal field splitting energy and depends[8] only on the parameters B and C. The value for the parameter Dq could be evaluated with the help of curve transition energies vs Dq, given by Orgel[9] using the energy level due to transition $^6A_{1g} \rightarrow ^4T_{1g}$ (^4G). The value for parameter Dq could not be obtained using the transitions $^6A_{1g} \rightarrow ^4E_g$, $^4A_{1g}$ (^4G) and $^6A_{1g} \rightarrow ^4E_g$ (^4D), because these transitions are independent of Dq, with almost zero slope. Parameter B and C are linear combination of certain coulomb and exchange integral and are generally treated as emperical parameters obtained from the spectra of the free ions. Slater-Condon-Shortly parameter F_2 and F_4 are related to Racah interelectronic repulsion parameter B and C as follow[10] : $B = F_2 - 5F_4$ and $C = 35F_4$. By using values of Racah parameter B and C, values for parameter F_2 and F_4 have been calculated (Table 2).

The electron-electron repulsion in complex is less than in the free ion, resulting in an increase distance between electrons and thus an effective increase in the size of the orbitals. On increasing delocalization the β decreases and is less than one in complex. Estimate of β has been obtained from the nephelauxetic parameter for ligand (h_x) and nephelauxetic parameter of the metal ion (K_M) as[11] : $(1-\beta)=h_x \cdot K_M$. The values for parameter h_x for the complex have been calculated using covalency-contribution of manganese(II) ion (0.07), while the numerical value 786 cm^{-1} for parameter B of free Mn^{2+} ion[7] is used to calculated value for the β. It has been observed that the lower value of β and higher value of h_x for mixed ligand complexes as

TABLE 2– EXPERIMENTAL TRANSITION ENERGIES, CALCULATED VALUES FOR PARAMETERS B, C, F_2, F_4, Dq (IN cm^{-1}) β AND h_x

Complex	$^6A_{1g} \rightarrow {}^4T_{1g}(^4P)$	$^6A_{1g} \rightarrow {}^4E_g(^4D)$	$^6A_{1g} \rightarrow {}^4E_g, {}^4A_{1g}(^4G)$	$^6A_{1g} \rightarrow {}^4T_{1g}(^4G)$	B	C	F_2	F_4	Dq	β	h_x
$[Mn(tu)_4(H_2O)_2]Cl_2$	32258	29411	24390	20618	717.0	3444	1194	95	763	0.91	1.25
$[Mn(tu)_4(py)_2]Cl_2$	27855	24875	24875	20000	425.7	4123	1034	117	850	0.54	6.54
$[Mn(tu)_4(phen)]Cl_2$	33557	27777	24271	19801	500.8	3852	1050	110	873	0.63	5.18
$[Mn(tu)_4(bipy)]Cl_2$	32786	28169	23809	19607	622.8	3516	1124	100	895	0.79	2.96
$[Mn(tu)_4(qu)_2]Cl_2$	32786	28818	24096	19801	674.5	3470	1170	99	873	0.85	2.02
$[Mn(tu)_4(ani)_2]Cl_2$	33333	28328	24096	20000	604.5	3610	1120	103	850	0.76	3.92
$[Mn(tu)_4(en)]Cl_2$	33003	27932	24154	19531	539.7	3751	1075	107	901	0.68	4.47

compared to the parent complex indicate the increase in covalent character on further complexation. Like other octahedral manganese(II) complexes the complexes studied in the present work yield light coloured solution with weak intensity in solution indicating most probably the octahedral environment around metal ion.

The infrared spectrum of the parent complex has confirmed the presence of coordinated water molecules by a band at 3460 cm^{-1}, whereas, the mixed ligand complexes derived from it donot show absorption in this region, indicating the replacement of coordinated water molecules by second ligand or ligands.

The S→M bond formation is expected to increase the contribution of the highly polar structure $\begin{matrix} H_2N \\ H_2N \end{matrix}{>}C\text{-}S^-$ to the thiourea molecule. This naturally will result in the greater double bond character for the N-C bond, while at the same time C-S bond will attain greater single bond character[13]. The high frequency medium-strong-NH absorption bands in the spectrum of thiourea shift to higher frequency region and the strong band observed at 730 cm^{-1} in thiourea shifts to lower frequency region on complexation support the sulfur coordination of thiourea ligand[18]. The strong band occurring at 1617 cm^{-1} in thiourea assigned to-NH_2 deformation ; shifts to 1600 cm^{-1} in the complex. The intense band occurring at 1413 cm^{-1} in thiourea is assigned to-NH_2 rocking. The N-C-N stretching vibration of thiourea molecule which is shown in the form of absorption around 1473 cm^{-1} moves to higher frequency region (1480 cm^{-1}) indicating most probably the greater double bond character of C-N bond on complex formation. The intensity of the strong absorption band at 1083 cm^{-1} in thiourea diminishes on the complex formation. This is most probably due to the considerable change in the nature of the N-C bond and C=S bond on coordination of thiourea through sulfur atom[14,16]. A band ~410 cm^{-1} in complexes correspond to a band at 411 cm^{-1} in thiourea may be assigned to-NH_2 torsional. The significant IR bands due to coordinated thiourea in different complexes are summarized in Table 3. In addition to the bands due to coordinated thiourea ligand the position of bands of the second ligand present in mixed ligand complexes are also modified on complexation showing their coordination to the metal atom.

TABLE 3 – SIGNIFICANT IR BANDS (IN cm^{-1}) DUE TO COORDINATED THIOUREA AND THEIR ASSIGNMENT

Thiourea	$[Mn(tu)_4(H_2O)_2]Cl_2$	$[Mn(tu)_4(py)_2]Cl_2$	$[Mn(tu)_4(phen)]Cl_2$	$[Mn(tu)_4(bipy)]Cl_2$	$[Mn(tu)_4(qu)_2]Cl_2$	$[Mn(tu)_4(ani)_2]Cl_2$	$[Mn(tu)_4(en)]Cl_2$	Assignment
3365s	3375s	3380s	3380m	3382m	3360s	3385s	3380s	
3260s	3285s	3275m	3290s	3280s	3280m	3280s	3260m	-NH_2 strech
3156s	3180s	3190s	3165m	3160m	3160s	3190s	3180s	vibrations
1617s	1600s	1607s	1610s	1600m	1612m	1607s	1614m	-NH_2 deformation
1473s	1480m	1478s	1481w	1479s	1478s	1485s	1480s	-C-N asym. strech
1413s	1442w	1450m	1422s	1438m	1435m	1445w	-	-C=S sym. strech
	1390s	1395m	1390m	1400sh	1387m	1392s	1375m	
1086s	1090m	1080m	1105m	1102m	1095w	1095w	1120w	-NH_2 rock
730s	720s	725m	718s	720s	718m	718s	715w	-C-N-sym. strech
411m	409w	410w	415m	408m	412w	410w	410w	-NH_2 torsional

Acknowledgement

We wish to thank the University Grants Commission, India, for its support through Grant and Fellowship (to D.S.S.) and Prof. R.C. Kapoor for providing necessary laboratory facilities.

References

1. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, John Wiley, New Delhi, 1967, p. 836.
2. L. J. Boucher and C. G. Coe, *Inorg. Chem.*, 1975, **14**, 1289.
3. L. H. Vogt, Jr., A. Zalkin and D. H. Templeton, *Inorg. Chem.*, 1967, **6**, 1725.
4. A. I. Vogel, A Text Book of Quantitative Inorganic Analysis, English Language Book Soc., London, 1971, p. 536.
5. R. J. Colline and L. F. Larkworthy, *J. Inorg. Nuclear Chem.*, 1975, **37**, 334.
6. B. N. Figgis and J. Lewis, *Prog. Inorg. Chem.*, 1964, **6**, 102.
7. L. J. Heidt, G. F. Koster and A. M. Johnson, *J. Amer. Chem. Soc.*, 1958, **80**, 6471.
8. C. Preti and G. Tosi, *Aust. J. Chem.*, 1976, **20**, 543.
9. L. E. Orgel, *J. Chem. Phys.*, 1955, **23**, 1004.
10. J. E. Huheey, Principles of Structure and Reactivity, Harper and Row, New York, 1972, p. 363.
11. C. K. Jorgenson, Oxidation Number and Oxidation States, Springer, New York, 1969, p. 106.
12. A. Yamaguchi, R. B. Penland, S. Mizushima, T. J. Lane, C. Curran and J. V. Quagliano, *J. Amer. Chem. Soc.*, 1958, **80**, 527.
13. R. A. Bailey and T. R. Pearson, *Canad. J. Chem.*, 1968, **46**, 3119 and references therein.
14. G. F. Svatos, C. Curran and J. V. Quagliano, *J. Amer. Chem. Soc.*, 1955, **77**, 6159.
15. D. G. Karraker, *J. Inorg. Nuclear Chem.*, 1969, **31**, 2833.

J. Indian Chem. Soc.,
Vol. LVII, March 1980, pp. 304-305

Extractive Spectrophotometric Determination of Cobalt as a Mixed Thiocyanate-Promethazine Complex

P. G. RAMAPPA, H. SANKE GOWDA and S. MANJAPPA

Department of Post-graduate Studies and Research in Chemistry, University of Mysore, Manasagangotri, Mysore-570 006, India

Manuscript received 12 July 1979, revised 15 November 1979, accepted 20 December 1979

A new spectrophotometric method for the determination of traces of cobalt based on the extraction of blue cobalt-thiocyanate-promethazine ion-association complex into chloroform from 1.5-4.5*M* sulphuric acid medium is described. Beer's law is valid over the concentration range 0.5-45 ppm of cobalt(II). The complex which is stable for over a week has an absorption maximum at 618-616 nm and its molar absorptivity is 1.39×10^3 l $mole^{-1}$ cm^{-1}. Many common ions do not interfere. The proposed method offers higher sensitivity than that of the classical reaction with thiocyanate and can be used in media of wider range of acidity and no problems arise from instability.

SANKEGOWDA *et al.*[1] proposed promethazine hydrochloride (PH) as redox indicator for vanadametry. Cavatorta[2] employed the reaction of palladous chloride with PH for the colorimetric determination of the latter. This paper deals with the extraction of cobalt-thiocyanate with PH in chloroform and its subsequent spectrophotometric determination in the organic phase.

Experimental

Appadatus :

Beckman Model DB spectrophotometer with matched 10 mm quartz cells was used for absorbance measurements. A *p*H meter Model LI-10 (ELICO, Hyderabad) was used for determining *p*H of the aqueous phase.

Reagents :

Standard cobalt (*II*) *solution* : A stock solution of cobalt (II) was prepared by dissolving cobalt (II) sulphate heptahydrate (AnalaR) in doubly distilled water and was standardised complexometrically[3]. The working solutions were made by suitable dilution of this stock solution.

PH solution. 0.1*M* solution of PH in AnalaR chloroform was prepared.

2*M* aqueous solution of ammonium thiocyanate was prepared.

Diverse ions. Solutions of diverse ions of suitable concentrations were prepared using analytical grade reagents.

Procedure : Place the sample solution containing 56 to 440 μg of cobalt (II) in a separatory funnel. Add 4 ml of 10*M* sulphuric acid, 5 ml of 2*M* ammonium thiocyanate and distilled water to bring the total volume to about 20ml. Add 5 ml of 0.1*M* PH in chloroform and shake for 1 min. Transfer the blue coloured chloroform layer to a 10 ml volumetric flask. Extract the aqueous solution twice with 2 ml portions of chloroform. Combine the chloroform extracts in the same 10 ml volumetric flask and dilute to the mark with chloroform. Measure the absorbance at 622 nm against a reagent blank prepared in the same way. Calculate the cobalt concentration of the sample solution by means of a calibration curve.

Results and Discussion

PH forms an intensely blue ion-association complex with the binary cobalt-thiocyanate complex in 1.5-4.5*M* sulphuric acid solution. The ion-association complex can be extracted into chloroform while the binary cobalt-thiocyanate complex cannot be extracted under the experimental conditions. The conditional extraction constant of the ternary complex was determined by the modified method of isomolar series[4]. The mean value of log K_E' was 4.68 ± 0.05, indicating good extraction with chloroform. The chloroform extract of the cobalt-thiocyanate-PH ion-association complex has an absorption maximum at 618-626 nm (Fig. 1). The reagent blank in chloroform does not show any absorption in the region 500-700 nm. Hence all absorbance measurements were made at 622 nm.

The effects of concentration of mineral acids, ammonium thiocyanate and PH were studied. The absorbance remained constant in 20 ml of 1.5-4.5*M* sulphuric or hydrochloric acid solution containing 2.5-10 ml of 2*M* ammonium thiocyanate and 3-8 ml

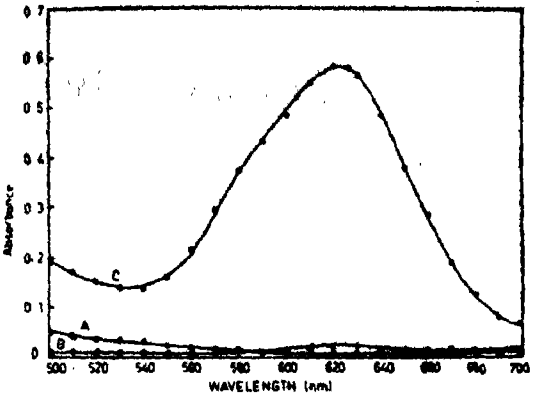


Fig 1. Absorption spectra of A PH B Co(II)-SCN complex, and C: Co(II)-SCN-PH complex [PH]=0.05M ; [Co] = 25 ppm.

of 0.1*M* PH in chloroform. Hence the optimum concentration of 2*M* H_2SO_4 or HCl, 5 ml of 2*M* ammonium thiocyanate and 5 ml of 0.1*M* PH in chloroform were selected for the determination of cobalt.

Range and sensitivity : Beer's law was obeyed in the range 0.5-45 ppm, with an optimum working range of 5.6-44 ppm of cobalt. The molar absorptivity was 1.39×10^3 l. $mole^{-1}cm^{-1}$ and the Sandell sensitivity was 42 ng of Co cm^{-2}. The sensitivity of the proposed method is higher than that of thiocyanate[4], pyrazoline derivatives[6], thiocyanate-1-phenyl-4-phenylamino-1, 2, 4-triazolium chloride[7] and thiocyanate-tetraphenyl arsonium salts[8]. The absorbance readings remained constant for over one week and were insensitive to temperature in the range 5-45°.

Effect of diverse ions : Several cations and anions were examined by applying the method to fixed amounts of cobalt in the presence of increasing quantities of the ions being studied. The tolerance limits for various diverse ions (Table 1) represent the concentration of foreign ions in the presence of which the absorbance of colalt-thiocyanate-PH complex solution obtained was within ±2% of the expected value.

Composition of the complex : The ratio of cobalt to thiocyanate and PH was determined by Job's method of continuous variations[9]. Since three components are involved in the formation of the extractable complex, two series of experiments were carried out by keeping one constant and varying the other constituent. The result obtained indicated that the mole ratio of Co(II) to SCN^- is 1 : 3 and of Co(II) to PH is 1 : 1. The mole ratio method[10] confirms the ratio of Co(II) to PH as 1 : 1.

TABLE 1—EFFECT OF DIVERSE IONS ON THE DETERMINATION OF COBALT
(Amount of cobalt taken = 15 ppm)

Ion added	Tolerance limit (ppm)	Ion added	Tolerance limit (ppm)
Na(I)	6000	Ce(IV)	65
K(I)	6000	Ti(IV)	40
Ca(II)	6000	V(V)	500
Mg(II)	6000	Pd(II)	250
Ba(II)	6000	Rh(III)	500
Zn(II)	500	Ir(III)	400
Cd(II)	6000	Ru(III)	2
Pb(II)	6000	Pt(IV)	600
Al(III)	4000	Os(VIII)	50
Bi(III)	250	Fluoride	5000
Cu(II)	50	Chloride	1000
Ag(I)	500	Bromide	3000
Au(III)	100	Iodide	4000
Cr(III)	100	Sulphate	15000
Fe(III)	1	Phosphate	10000
Mn(II)	6000	Nitrate	5000
Mn(VII)	100	Carbonate	1000
Ni(II)	500	Thiosulphate	6000
Cr(VI)	25	Oxalate	15000
Mo(VI)	5	Citrate	15000
W(VI)	25	Tartrate	15000
U(VI)	1000	Acetate	15000
Zr(IV)	10		

Acknowledgement

The authors thank M/s British Pharmaceutical Laboratories, Bombay and M/s May and Baker Ltd., Bombay for the supply of PH. One of the authors (S. M.) is grateful to the Council of Scientific and Industrial Research, New Delhi, for the award of a Junior Research Fellowship.

References

1. H. SANKE GOWDA, R. SHAKUNTHALA and P. G. RAMAPPA, *Talanta*, 1968, **15**, 266.
2. L. CAVATORTA, *J. Pharm. Pharmacol.*, 1959, **11**, 49.
3. A. I. VOGEL, "A Text-book of Quantitative Inorganic Analysis" The ELBS and Longmans, London, 1975, p. 443.
4. W. LIKUSSAR and D. F. BOLTZ, *Anal. Chem.*, 1971, **43**, 1265, 1273.
5. E. B. SANDELL, "Colorimetric Determination of Traces of Metals", 3rd ed. Interscience, New York, 1959, p. 423.
6. E. V. SOKOLOVA, A. C. PESIS and N. I. PANOVA, *Zh. Anal. Khim.*, 1957, **12**, 489.
7. C. CALZOLARI and L. FAVRETTO, *Analyst*, 1968, **93**, 494.
8. H. E. AFFSPRUNG, N. A. BARNES and H. A. POTRATZ, *Anal. Chem.*, 1951, **23**, 1680.
9. P. JOB, *Ann. Chim.*, 1928, 9, 113.
10. J. H. YOE and A. L. JONES, *Ind. Eng. Chem, Anal. Ed.*, 1944, **16**, 111.

J. Indian Chem. Soc.,
Vol. LVII, March 1980, pp. 306-308

*p*H and Sorption of Mono-Nitrophenols by Alumina. Part. IV

G. L. MUNDHARA, M. P. TIWARI

Department of Chemistry, Govt. College of Science, Raipur (M. P.)

and

J. S. TIWARI*

Department of Chemistry, Govt, Girl's College, Raipur (M.P.). 492-001, India

Manuscript received 15 October 1979, accepted 30 December 1979

Change in the sorption behaviour of *o*-, *m*- and *p*- nitrophenols with chromatographic alumina of varying surface *p*H (*p*H 3.5-11.5) in non-aqueous systems has been investigated. The enhanced adsorption with *p*H, desorption behaviour and liquid-solid adsorption chromatography (LSAC) of the solutes is described.

HYDRONIUM-ION concentration has been found to be a significant factor in the adsorption of various organic compounds by alumina[1-4]. In continuation of our work[3,4], attention is now focussed on the nature of sorption of *o*-, *m*-and *p*-nitrophenols on Brockmann alumina, pretreated with HCl-acid and aq. caustic soda. The pertinent literature[5-8] shows that possibly no work has been made on the lines described in this paper.

Experimental

Substrate :

Brockmann alumina (S. Merck, India), pretreated with HCl-acid* and aq NaOH of varying strengths, has been used as substrate. The procedure adopted for the preparation of basic alumina samples is summarised in Table 1.

Reagents and Apparatus :

The solutes, *o*-, *m*- and *p*-nitrophenols (to be shown as ONP, MNP and PNP) were the BDH products, which were recrystallised with ethanol and water (ONP), toluene (MNP) and water (PNP). The solvents used were the AR BDH products which were distilled before use.

"Systronics" *p*H meter (Type 322, accuracy $\pm$ 1%) and "Spekol spectrocolorimeter" (Carl-Zeiss) were used for measurements. The glass apparatus used were of corning/pyrex make, and calibrated before use.

All the experiments were done at $30 \pm 1°$.

Procedure :

Weighed amounts (0.25 g) of alumina of specific

TABLE 1—CONDITIONS FOR THE PREPARATION OF BASIC ALUMINA SAMPLES

Initial amount of alumina : 100 g (*p*H 8.6)
Time of contact after shaking: 10 min.

*p*H of alumina prepared	*p*H of alumina initially taken	Volume of aq NaOH added	Period of mechanical shaking	*p*H of the wash-liquid.
9.5	8.6	200 ml of 0.02 *N*-NaOH.	50 min.	10.0-10.5
10.0	8.6	200 ml of 0.1 *N*-NaOH.	20 min.	10.5-11.0
10.6	8.6	200 ml of 0.1 *N*-NaOH.	50 min.	11.2-11.8
11.5	10.6	200 ml of 2 *N*-NaOH.	50 min.	-*

*-*p*H of the wash-liquid was not determined, since the *p*H was above 12.

pH were taken in well-stoppered 25-ml volumetric flasks. These were then shaken with nitrophenol solution (25 ml each) of known concentrations for 24 hours at 30±1° in a thermostat. After attainment of equilibrium, the equilibrium concentrations of the solutes in dioxane and methanol were estimated colorimetrically at 400 nm by developing colour with aq NaOH.

The benzene solutions of the nitrophenols were poured on water containing the alkali, the solvent evaporated on water bath, and estimated colorimetrically.

Desorption studies of the solutes adsorbed on alumina were carried out as described earlier[8].

Results and Discussion

The results of adsorption are shown in Table 2 and presented graphically in Figs. 1 and 2. Using alumina of various surface pH as substrate, it is observed that :

i) From dioxane solution, the favourable range of adsorption of PNP is pH 6.0-11.5. MNP is not adsorbed at all by the substrates. ONP hardly shows 10% adsorption in the pH range 6.0-8.6 which increases to 15% at pH11.5 (Table 2).

ii) The solutes are quantitatively adsorbed from benzene at pH 3.5-11.5 within 5 minutes.

iii) From methanol, PNP (pH 6.0-8.6) and ONP (pH 3.5-8.6) show some adsorption but MNP has no affinity for the substrates.

iv) Under the dilutions taken, the compounds have negligible adsorption from water.

TABLE 2—pH AND ADSORPTION OF MONO-NITROPHENOLS FROM DIOXANE AND METHANOL. (30±1° C, 24 hrs)

Solvent	Initial concentration (mg/l).	pH of alumina and amount adsorbed (mg/l/g). pH 3.5 PNP	ONP	pH 6.0 PNP	ONP	pH 8.6 PNP	ONP	pH 11.5 PNP	ONP
Dioxane	80.0	2.5	No adsorption	20.5	No adsorption	21.7	5.5	48.0	6.4
	60.0	1.9		15.5		16.5	1.2	38.0	6.0
	40.0	1.5		14.3		14.8	1.0	28.0	4.5
	30 0	1.4		14.0		14.0	0.8	22.6	3.5
	20.0	1.3		10.5		10.5	0.5	16.0	2.0
	10 0	0.6		5.5		5.5	-	8.6	0.5
Methanol	80.0	No adsorption	3.7	11·7	8.8	8.0	7.2	No adsorption	No adsorption
	60.0		3 2	10·0	8.8	7.0	7.0		
	40.0		1.5	7.4	6.0	4.7	6.0		
	30.0		0.8	6.0	4.5	3.6	4.0		
	20.0		0·5	4.3	3.0	2.5	3.0		
	10.0		-	2.5	1.0	1.2	1.0		

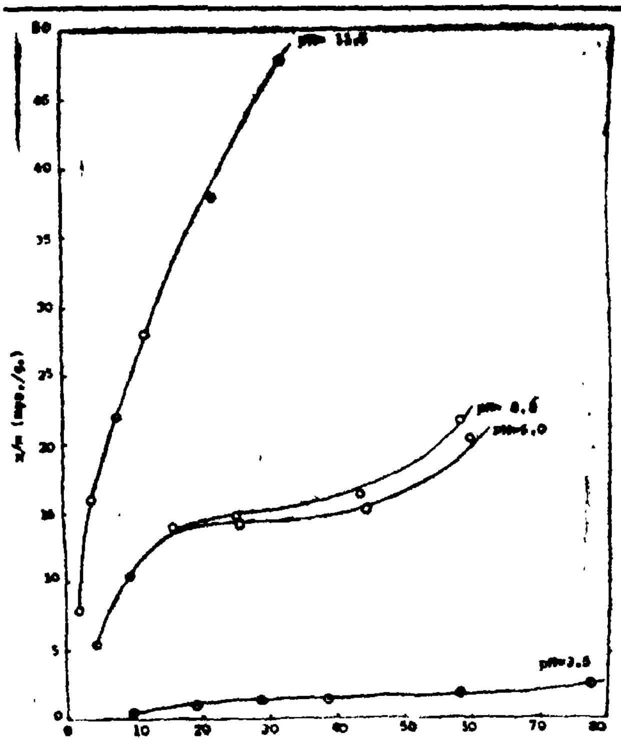


Fig. 1. Adsorption isotherms of p-nitrophenol from solution in dioxane on alumina of varying pH.

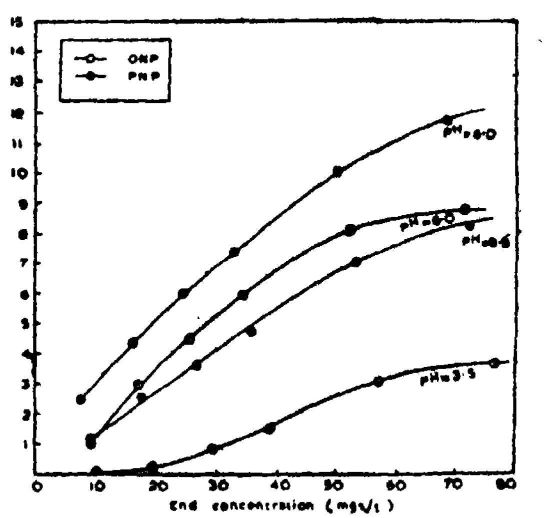


FIG 2 Adsorption isotherms of PNP and ONP from methanol soln. on alumina of varying pH.

v) The desorption data (not shown separately) reveal that the mono-nitrophenols adsorbed on alumina from benzene could be desorbed sufficiently with methanol. Thus PNP, MNP and ONP could be desorbed to the extent of 80%, 75% and 60% respectively.

vi) The solutes adsorbed from dioxane on alumina (*p*H 11.5) are desorbed quantitatively with water and 0.1 *N* aq. NaOH.

The pKa of these sorbates lies in the range 7.0-8.5 (PNP 7.20, MNP 8.40 and ONP 7.17). It means that at *p*H<7.0, the molecular species of the solutes should predominate in solution and at pH >7.0 mainly the anions should be involved in adsorption. As *p*H of the substrate increases above the pKa value, more of the anionic species are generated, which are not soluble in the non-aqueous solvents (dioxane, benzene) and hence adsorbed.

The isotherms for ONP and PNP are of L-and S-shape (Figs. 1 and 2). PNP from dioxane at *p*H 11.5 has L_1-type isotherm which assumes rather S-shape at *p*H 6.0-8.6. ONP also gives S-type curve from dioxane at *p*H 11.5 (not shown). Thus, the mechanism of adsorption may well differ according to the history of alumina surface[8].

It is likely that weak chemical interactions may occur between the free-OH groups of alumina surface and the anionic species in the favourable range of adsorption (*p*H>7.0). At *p*H values below their pKa, solute-solute interactions (e.g., hydrogen bonding) may occur affecting adsorption. This is also indicated by the change in the nature of isotherms from L-to S-type.

The low affinity of ONP as compared to PNP may be due to chelation. The behaviour of MNP is rather typical, which needs further investigation.

Chromatographic Separation of ONP, MNP and PNP :

Our aim in the above short study has been to find out suitable conditions for the column chromatography of these isomeric nitrophenols. The separation is based on the quantitative adsorption of the compounds from benzene by alumina of *p*H 11 5 (Table 2), and the varying adsorption-desorption (and hence migration) with dioxane containing methanol.

Glass column (10×1 cm) was packed dry with Brockmann alumina of *p*H 11.5 to a column height of 8 cm 5.0 ml each of the nitrophenol solution in benzene (80 mg/l) were withdrawn, mixed, applied to the column, and kept as such for an hour. On developing the chromatogram with 30 ml of dioxane-methanol (19 : 1, v/v) three distinct bands could be seen upper canary-yellow band of PNP (0.5 cm width), colourless space (0.5 cm), light golden-yellow band of MNP (1 cm), colourless space (2 cm), and then the orange-yellow band of ONP (2 cm). This shows a clear-cut separation of the solutes. The separation was more distinct with further 10 ml of the developer. ONP could be removed with 20 ml of dioxane—methanol (9 : 1, v/v.) MNP was eluted out of the column with further addition of 30 ml of the eluent. PNP was eluted with 20 ml of dioxane-methanol (1 : 1, v/v). The eluate fractions were determined colorimetrically by developing colour with alkali, as described earlier.

The recoveries were quantitative for ONP and PNP and 99.9% for MNP.

Distribution studies and separation :

The distribution coefficients (Kd) for desorption of the solutes adsorbed from benzene were detemined (ml g^{-1}) after equilibrating alumina (0.25 g, *p*H 11.5) with 25 ml benzene solution (80 mg/l) for one hour at 30±1°. After draining out benzene completely, the adsorbed solutes were shaken with 25 ml of the eluent (mixture of dioxane-methanol of varying proportions) for 24 hr, and the desorbed quantity estimated colorimetrically. The values are shown in Table 3.

TABLE 3—Kd VALUES FOR ONP, MNP AND PNP.

Solute	Kd values, ml g^{-1}, in dioxane-methanol (v/v).		
	19:1	9:1	1:1
PNP	56.2	53.1	41.3
MNP	247.3	152.8	100.0
ONP	133.3	91.4	47.0

A review of Table 3 shows that MNP has the highest Kd value in the developer (19 : 1, dioxane-methanol). It is, therefore, expected that in the ternary separation, MNP should form the uppermost band of the chromatogram. However, it occupies the middle portion of the chromatogram, as described earlier. As per the adsorption behaviour, MNP is expected to occupy the lower-most band, as it has no adsorption in these solvents. Hence, the combined effect of the two forces of adsorption and desorption determine the migration rate. The effect is maximum on ONP.

References

1. L. R. SNYDER, *J. Chromatog.*, 1966, **23**, 388.
2. M. J. FULLER. *Chromatogr. Review*, 1971, **14**, 45.
3. G. L. MUNDHARA and J. S. TIWARI, *J. Indian Chem. Soc.*, 1978, **55**, 1033.
4. G. L. MUNDHARA and J. S. TIWARI, *J. Indian Chem. Soc.* (In press).
5. J. S. JAIN and V. L. SHOEYINK, *J. of Water Pollution Control*, 1973, **45**, 2463.
6. J. S. MATSON and H. B. MARK (Jr), *J. of Colloid and Interface Sci.*, 1969, **31**(1), 1916.
7. C. H. GILES, A. P. D'SILVA and A. S. TRIVEDI, *J. of Appl. Chem. (London)*, 1970, **20**, 37.
8. C. H. GILES, A. P. D'SILVA and I. A. EASTON, *J. Colloid and Interface Sci.*, 1974, **47**, 755.

J. Indian Chem. Soc.,
Vol. LVII, March 1980, pp. 309-311

Polarographic Behaviour of the Mixed Complexes Formed by Cd(II) with Gluconate-pyridine and Gluconate-itaconate Systems

L. K. AGARWAL and D. S. JAIN

Chemical Laboratories, University of Rajasthan, Jaipur-302 004 (India)

Manuscript received 27 February 1979, accepted 2 November 1979

Schaap and McMasters method has been used to determine the overall formation constants of mixed ligand complexes formed by (a) Cd(II) with gluconate and itaconate and (b) Cd(II) with pyridine and gluconate. DeFord and Hume's treatment showed that Cd(II) forms three complexes species each with pyridine, gluconate and itaconate ions. In both the mixed ligand systems the reductions were reversible and diffusion controlled involving two electrons. Cd(II) forms three mixed ligand species [Cd(X) (Y)] ; [Cd(X) $(Y)_2$] and [Cd$(X)_2$ (Y)] with :

(a) $\beta_{11}=34$; $\beta_{12}=333$; $\beta_{21}=1750$ [glu-ita] and (b) $\beta_{11}=467$; $\beta_{12}=667$; $\beta_{21}=1050$ [glu-pyr].

Tendencies of various complexes to add and substitute another ligand is discussed.

MIXED ligand complexes have been studied by potentiometric[1-2] and spectrophotometric measurements[3-4] and by pH titration curves[5]. Schaap and McMasters[6] have extended the technique of polarography by a logical extension of DeFord and Hume's[7] method by applying the latter to cases where a metal ion forms complex with two ligands simultaneously in solution.

The practical determination of stability constants involves many more measurements than the straight forward DeFord and Hume's approach and can be somewhat tedious. The mixed complexes of Cd(II) with various organic ligands have been studied in our laboratory[8-10]. It was found that Cd(II) forms 1 : 3 highest complexes with pyridine, gluconate and itaconate ions. Present paper deals with the mixed ligand studies of Cd(II) with (a) gluconate-itaconate and (b) gluconate-pyridine at d.m.e.

Experimental

Sodium gluconate, sodium itaconate and pyridine were used as complexing agents whereas $NaClO_4$ served as supporting electrolyte to maintain constant ionic strength [$\mu=1.5$]. All the measurements were carried out at 293 $\pm$.1°K which was maintained by Haake type ultrathermostat. The solution was placed in an H-type cell coupled with saturated calomel electrode through an agar-agar saturated with NaCl salt bridge. Prior to reduction at d.m.e., purified nitrogen gas streamed through the test solution for 20 minutes to expel the dissolved oxygen. The polarograms were obtained on a manual set up. The d.m.e. used has the following characteristics : $m=2.10$ mg/sec., $t=3.0$ seconds (at-1.0 V vs S.C.E. in 1*M* $NaClO_4$) was used throughout the course of investigation.

Results and Discussion

Cd(II) produces a single, well developed wave in each solution. The plots of i_d vs $\sqrt{h}$ (h=effective height of mercury column) are linear and pass through the origin. The plots of $\log \frac{i}{i_d - i}$ Vs E. were linear with a slope of 32+1 mV. Thus, the reduction was diffusion controlled and found reversible involving two electrons. The overall formation constants of simple complexes were determined by DeFord and Hume's method using the polarographic measurements. The results are summarised as below :

System	Overall formation constant		
	β_1	β_2	β_3
Cd(III)-Gluconate	5	39	200
Cd(II)-Pyridine	40	80	990
Cd(II)-Itaconate	20	160	1760

The polarographic characteristics and Fij function values of the mixed Cd(II)-itaconate-gluconate system at fixed gluconate concentrations of 0.2 and 0.3*M* are summarised in Table 1, whereas Table 2 presents the polarographic characteristics and Fij function values of the mixed Cd(II)-pyridine-gluconate system at fixed gluconate-concentrations of 0.2 and 0.3*M* respectively.

TABLE 1—POLAROGRAPHIC CHARACTERISTICS OF Cd(II)-ITACONATE-GLUCONATE-SYSTEM AT 293°K ($\mu = 1.5$)

*C_X	Gluconate ion concentration = 0.2*M* $E_{1/2}$ (-V vs S.C.E.)	i_d (μA)	$F_{00}(X)$	$F_{10}(X)$	$F_{20}(X)$	$F_{30}(X)$	Gluconate ion concentration = 0.3*M* $E_{1/2}$ (-V vs S.C.E.)	i_d (μA)	$F_{00}(X)$	$F_{10}(X)$	$F_{20}(X)$	$F_{30}(X)$
0	0.582	2.82	-	-	-	-	0.582	2.82	-	-	-	-
0.05	0.606	2.42	7.71	34.14	-	-	0.612	2.35	12.71	54.18	-	-
0.10	0.613	2.35	13.75	77.51	375	-	0.618	2.29	20.98	109.76	498	-
0.15	0.622	2.24	29.31	155.39	769	1793	0.626	2.20	40.97	206.52	976	1842
0.20	0·628	2.18	48.44	212.21	861	1805	0.631	2.05	64.64	273.22	1066	1830
0.25	0.633	2.07	75.67	278.67	954	1818	0.636	2.02	97.93	351.72	1167	1867
0.30	3.638	2.06	112.16	353.87	1046	1820	0.640	1.91	141.97	439.90	1066	1888
0.35	0.642	2.00	158.79	436.56	1133	1808	0.644	1.88	196.80	533.71	1351	1860

A = 6 ; B = 40 ; C = 500 ; D = 1810   A = 10 ; B = 60 ; C = 700 ; D = 1860

*C_X = Concentration itaconate ions in moles/litre.

TABLE 2—POLAROGRAPHIC CHARACTERISTICS OF Cd(II)-PYRIDINE-GLUCONATE SYSTEM AT 293°K ($\mu = 1.5$)

*C_X	Gluconate ion concentration = .2*M* $E_{1/2}$ (-V vs S.C.E.)	i_d (μA)	$F_{00}(X)$	$F_{10}(X)$	$F_{20}(X)$	$F_{30}(X)$	Gluconate ion concentration = 0.3*M* $E_{1/2}$ (-V vs S.C.E.)	i_d (μA)	$F_{00}(X)$	$F_{10}(X)$	$F_{20}(X)$	$F_{30}(X)$
0	0.582	2.82	-	-	-	-	0.582	2.82	-	-	-	-
0.1	0.622	2.38	27.66	176.6	-	-	0.625	2.09	39.88	248.8	-	-
0.2	0.630	2.24	55.02	225.1	325	-	0.633	1.95	79.96	323.7	419	-
0.3	0.638	2.09	110.97	336.6	588	995	0.640	1.80	150.74	452.5	708	1027
0.4	0.644	2.04	181.83	429.6	675	962	0.646	1.79	243.24	570.6	827	1066
0.5	0.649	1.95	281.78	543.6	768	956	0.651	1.75	367.41	704.8	930	1060
0.6	0.654	1.91	427.41	695.7	893	1005	0.655	1.63	541.05	876.8	1061	1102
0.7	0.658	1.84	606.76	852.5	987	999	0.659	1.60	756.74	1059.6	1170	1101

A = 10 ; B = 160 ; C = 290 ; D = 1000   A = 15 ; B = 240 ; C = 400 ; D = 1070.

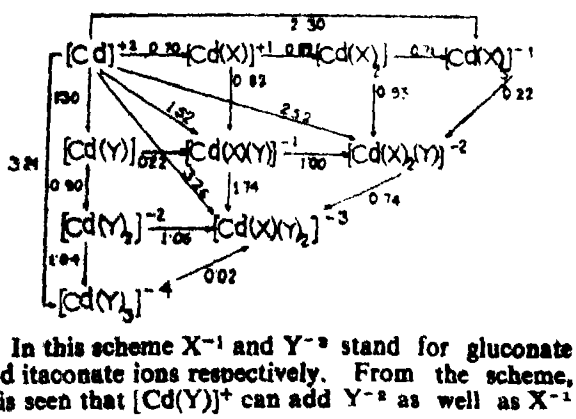
*C_X = Concentration of pyridine in moles/litre.

The composition and formation constants for the mixed ligand systems have been evaluated by Schaap McMasters' treatment which has been discussed in details earlier[8]. In both the systems, Cd(II) forms three mixed ligand species :

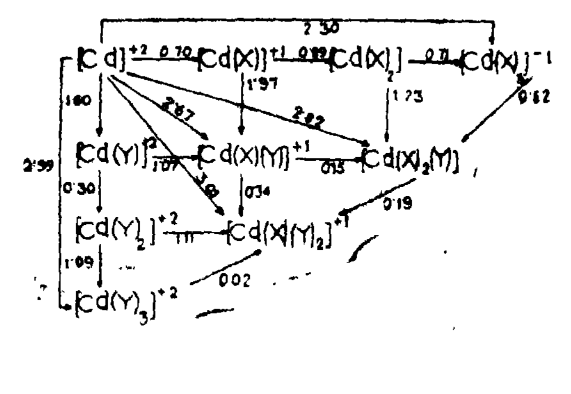
[Cd(X) (Y)] ; [Cd(X)$(Y)_2$] and [Cd$(H)_2$(X)] with :

(a) $\beta_{11} = 34$; $\beta_{12} = 333$; $\beta_{21} = 1750$ and
(b) $\beta_{11} = 467$; $\beta_{12} = 667$; $\beta_{21} = 1050$ respectively.

Cd(II) forms three mixed complexes, existing in solution having following equilibria. The numerical values represent log K[where K is the equilibrium constant of the step indicated in the summary].



In this scheme X^{-1} and Y^{-2} stand for gluconate and itaconate ions respectively. From the scheme, it is seen that $[Cd(Y)]^+$ can add Y^{-2} as well as X^{-1} but the results show that the addition of the latter is easier. The two unsaturated complexes $[Cd)X)]^{+2}$ and [Cd(Y)] can add Y^{-2} and X^{-1} respectively forming the mixed complex $[Cd(X) (Y)]^{-1}$. The relative tendencies of addition reveal that Y^{-2} is stronger ligand than X^{-1} (see the step constants). The unsaturated mixed complex $[Cd(X) (Y)]^{-1}$ can add itself X^{-1} as well as Y^{-2}. The addition of Y^{-2} is, however, easier than X^{-1}. [Cd(Y)] can add X^{-1} as well as Y^{-2} but the addition of Y^{-2} is easier than that of X^{-1}. This shows clearly that the mixed complex formation is preferred over the simple. Saturated simple complex $[Cd(X)_3]^{-1}$ can accommodate Y^{-2} in place of X^- to form $[Cd(X)_2(Y)]^{-2}$. Therefore, we conclude that in presence of two different ligands the metal ion preferably forms mixed complexes.



In this scheme (b) X^{-1} and Y represent gluconate and pyridine respectively. From the equilibrium constant values given in the scheme, we can discuss various relative tendencies of mixed complexation similarly.

Acknowledgement

The authors wish to express their gratitude to the C.S.I.R., New Delhi for the financial assistance.

References

1. J. I. WATTERS and J. MANSON, *J. Amer. Chem. Soc.*, 1956, **78**, 285.
2. G. SCHWARZENBACH and A. WILLI, *Helv. Chim. Acta*, 1951, **34**, 528.
3. L. NEWMAN and D. N. HUME, *J. Amer. Chem. Soc.*, 1957, **79**, 4571, 4581.
4. G. SCHWARZENBACH and J. HELLER, *Helv. Chim. Acta*, 1951, **34**, 1876, 1899.
5. J. I. WATTERS and DER. Witt, *J. Amer. Chem. Soc.*, 1960, **82**, 1333.
6. W. B. SCHAAP and D. L. MCMASTERS, *J. Amer. Chem. Soc.*, 1961. **83**, 4699.
7. D. D. DEFORD and D. N. HUME, *J. Amer. Chem. Soc.*, 1951, **73**, 5321.
8. D. S. JAIN and L. K. AGARWAL, *Indian J. Chem.* (Accepted).
9. D. S. JAIN, P. S. VERMA and L. K. AGARWAL, *J. Electrochem. Soc.* India, (Accepted).
10. D. S. JAIN and L. K. AGARWAL, *Trans., SAEST*, (Accepted).

J. Indian Chem. Soc.,
Vol. LVII, March 1980, pp. 312-314

Kinetics and Mechanism of the Reaction Between Dihalodicarbonylrhodate[I] Anions and Pyridine

F. H. JUMEAN

Department of Chemistry, University of Jordan, Amman, Jordan

Manuscript received 16 August 1979, accepted 30 December 1979

The kinetics of the reaction between dihalodicarbonylrhodate(I) anions of the formula $[RhX_2(CO)_2]^-$, where X = Cl, Br, I, and pyridine was followed spectrophotometrically and the effect of temperature on the rate constants was investigated. The reaction was found to obey a second order rate expression, first order in each of the complex anion and pyridine. The rate constants follow the decreasing order I > Br > Cl. A mechanism is proposed to account for these observations.

THE 4-coordinate complexes of rhodium (I) are of the d^8 square planar type[1]. They are noted for their ability to undergo oxidative addition reactions with a variety of ligands, leading to the formation of d^6 octahedral complexes[2]. The carbonyl complexes or rhodium (I) are particularly interesting because of the Rh-CO bond. The strength of this bond, as indeed is the case for many other metal carbonyl bonds, is believed to originate from a synergetic effect produced by (i) the donation of the lone electron pair on CO to the metal, and (ii) the back donation of electrons from the non-bonding d orbitals of rhodium to the antibonding orbitals of CO[3]. The net effect is to strengthen the Rh-CO bond, conferring upon it a double bond character, and to reduce the bond order of CO in the complex. A verification of this effect is furnished by infrared spectral data[4] which show sizable shifts in the stretching frequencies of Rh-CO and CO bonds. Thus, reactions involving the departure of such a metal liganded carbonyl proceed slowly because of the synergetic effect. The departure of a second liganded carbonyl would take place even more slowly because the d electrons on the metal would now be more available for the strengthening of the remaining metal-CO bond. In rhodium (III) complexes, however, the Rh-CO bond is much weaker than that in rhodium (I) complexes, because of the decreased availability of electrons for back donation.

The dihalodicarbonylrhodate (I) anion, $[RhX_2(CO)_2]^-$, where X = Cl, Br, I, has a cis square planar geometry[4]. When an ethanolic solution of this anion is reacted with pyridine (py) the product[5] formed is the octahedral complex trihalotris (pyridine) rhodium(III). The infrared spectrum[5] of this complex suggests that this product is a mixture of two isomers. In this work, the kinetics of this reaction, for all three halo analogues, was followed and the temperature effect, for the purpose of obtaining activation parameters, was investigated. The aim is to postulate a mechanism which would answer the question as to whether the departure of CO occurs before or after the oxidation of Rh(I) to Rh III), to determine at what stage in the course of the reaction does the addition of pyridine take place, and to shed some light on the role played by the halogen ligands.

Experimental

Materials : Rhodium trichloride was purchased in the hydrated form from Johnson Matthey Chemicals, Ltd., England. Carbon monoxide was generated by reacting formic acid with concentrated sulfuric acid. All other materials were of A.R. grade and were used without further purification.

Preparation of Compounds : The dichlorodicarbonylrhodium (I) anion, $[RhCl_2(CO)_2]^-$, was prepared by refluxing an ethanolic solution of hydrated rhodium trichloride (0.2 g in 30 ml) with carbon monoxide for about five hours with continuous stirring[6]. During this time the color changed from dark red to pale yellow. Th- bromo and iodo analogues were prepared by metathesis[4,7]. The product in each case was isolated and purified according to the method described by Kingston *et al*[5]. Infrared spectra taken for the solutions agreed closely with literature values[4].

Instrumentation : A Unicam SP 8000 spectrophotometer, fitted with a thermostated cell compartment. was employed for monitoring all reactions. The wavelength calibration was verified by taking a spectrum for holium oxide. Infrared spectra were recorded on a Perkin-Elmer 257 grating spectrophotometer.

Rate measurements : The reaction rate for the chloro and bromo analogues with pyridine was followed at 350 nm and that for the iodo analogue

at 386 nm. All solutions were thermostated for at least 20 minutes prior to mixing. The reference cell in each case contained the solvent, absolute ethanol, to which was added the necessary amount of pyridine needed to make its concentration identical in both cells. For the purpose of studying the effect of temperature, measurements were made in the temperature interval 15-45°. For each individual run, the equilibrium absorbance value, Ae, was obtained either several hours after mixing or the following day.

Results

Absorbance values were obtained at 25.0° as a function of time for several ethanolic solutions containing equimolar concentrations of $[RhCl_2(CO)_2]^-$, ($5.10 \times 10^{-4} M$) and varying concentrations of pyridine (0.11-2.48 *M*). The linearity of the log $(A_t - A_e)$ vs. time plots indicates that the reaction is first order with respect to time (A_t and A_e are the absorbance values at time t and at equilibrium, respectively). Form the slope of each line, an apparent first order rate constant, k'_1. was calculated. When the k'_1 values were plotted as a function of pyridine concentration, a fairly linear plot was obtained indicating that the reaction is first order with respect to pyridine. The reaction thus obeys a second order rate expression, first order with respect to each of pyridine and the complex anion. The observation that a pseudo-first order rate law is operative ought not to be surprising in view of the large stoichiometric excess of pyridine. The second order rate constant, k_2, as calculated from the slope of this plot has the value of 1.93×10^{-2} liter mole^{-1}min^{-1}.

The kinetic behaviour for the reactions of the bromo and iodo analogues with pyridine was investigated in the same manner and the rate law was found to be identical for all the three analogues. The second order rate constants for the bromo and iodo analogues were found to have the values of 4.10×10^{-2} and 9.95×10^{-2} litre mole^{-1} min^{-1} respectively.

In view of these results the emperical rate expression, satisfying all three reactions, may be written as

$$-[dRhX_2(CO)_2]^-/dt = k'_1[RhX_2(CO)_2]^- = k_2[py][RhX_2(CO)_2]^- \quad ...(1)$$

This rate expression was further verified by varying the concentration of the complex ion, for all three reactions, over an approximately tenfold range, while maintaining a constant initial concentration of pyridine (1.30*M*). Plots of the initial rate vs. the concentration of the complex ion initially present were linear in each case, confirming that the reaction is first order with respect to the complex ion. Furthermore, the slopes of these plots were fairly nearly identical with the k'_1 values expected at this concentration of pyridine.

Effect of temperature: The effect of temperature on the second order rate constant was investigated for all three reactions. The data were plotted according to the Eyring equation :

$$k_2 = (kT/h) \exp(\Delta \overset{*}{S}/R) \exp(\Delta \overset{*}{H}/RT) \quad ...(2)$$

The activation parameters $\Delta\overset{*}{H}$ and $\Delta\overset{*}{S}$, as calculated from the slope and intercept of a plot $\ln(k_2/T)$ vs T respectively, are given in Table 1.

TABLE - 1

X	ΔH^*,kcal/mole	ΔS^*,cal deg^{-1}mole^{-1}
Cl	11.2	-37.0
Br	8.71	-43.7
I	6.23	-50.4

Discussion

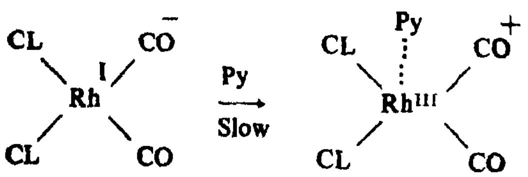
The results of this investigation indicate that only one of the three pyridine molecules incorporated in the final product, $[RhX_2Py_3]$, is involved in the rate determining step. Now if the reaction were to follow a bimolecular displacement (SN_2) mechanism, with the approach of a pyridine molecule leading to the synchronous departure of a carbonyl, then the second order rate constants associated with the complex anions should be highest for the chloro, and lowest for the iodo, analogues. This is because the Rh-C bond order, as evidenced by infrared measurements[4], is highest for the iodo, and lowest for the chloro, analogue. This is readily explained on the basis that the most electronegative halogen, chlorine in this case, would be most efficient in withdrawing electrons away from the Rh-C bond, thereby reducing its double bond character.

On the basis of the above argument, it may be concluded that the rate determining step does not involve the departure of a carbonyl group. This conclusion is further supported by two additional pieces of evidence : (i) The high negative $\Delta\overset{*}{S}$ values obtained in this work suggest a transition state more restricted than that encountered in typical SN_2 reactions. Since tetragonal pyramidal complexes of rhodium are known[5], it seems reasonable to postulate this geometry for the activated complex, with a pyridine molecule occupying the apex. From these values, moreover, it may be concluded that the iodo analogue is associated with the most restricted transition state and hence the shortest Rh-py bond. (ii) Although no values for Rh-C bond energies in Rh (I) complexes are available, the

ΔH^{*} values obtained are quite lower than would be expected for a metal carbon bond with a partial double bond character. Furthermore, even if is assumed that the ΔH^{*} values correspond to bond energies, this assumption falls apart because it would be inconsistent with the evidence[4] that the Rh-C bond is strongest for the iodo, and weakest for the chloro, analogue.

On the other hand, electron rich central atoms should be more susceptible to the loss of an electron pair than their electron deficient counterparts. Since the electron density on rhodium in $[RhX_2(CO)_2]^-$ would be highest for the iodo, and lowest for the chloro, analogue, i.e. opposite to the trend in electronegativity, it follows that the oxidation of Rh(I) to Rh (III) ought to be fastest for the iodo, and slowest for the chloro, analogue. This leads to the suggestion that the oxidation step is probably synchronous with the addition of the first pyridine molecule. This seems more plausible when considering that the tetragonal pyramidal geometry proposed in this work is normally associated with Rh (III) rather than Rh (I) complexes[1].

The above arguments lead to the postulation of the following mechanism :



Tetragonal Pyramid

$$\xrightarrow[\text{X}^- \\ \text{Fast}]{2\text{Py}} Rh^{III}X_2Py_2$$

2 Octahedral isomers

It may be noted that the second (fast) step probably involves two fast steps, one for the removal of each carbonyl group.

Acknowledgement

The author wishes to thank the University of Jordon for financial support and Mr. Y. A. Asha for performing some of the measurements.

References

1. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, John Wiley & Sons, Inc., New York, third edition, 1972, p. 1018.
2. J. A. Osborn, F. H. Jardine, J. F. Young and G. Wilkinson, *J. Chem. Soc.*, A, 1966, 1711.
3. F. Basolo and R. G. Pearson, Mechanisms of Inorganic Reactions, John Wiley & Sons, Inc., New York, second edition, 1977, p. 535.
4. L. M. Vallarino, *Inorg. Chem.*, 1965, 4, 2, 161.
5. J. V. Kingston, F. T. Mahmoud and G. R. Scollary, *J. Inorg. Nuclear Chem.*, 1972, 34, 3197.
6. J. Chatt and B. L. Shaw, *J. Chem. Soc.*, A, 1966, 1437.
7. M. K. Fayyad, dissertation, University of Jordan, 1974.
8. S. J. Laplaca and A. Ibers, *Inorg. Chem.*, 1966, 5, 405.

J. Indian Chem. Soc.,
Vol. LVII, March 1980, pp. 315- 317

Kinetics and Mechanism of the Oxidation of N-Methylmorpholine by Alkaline Hexacyanoferrate[III] Ion

BHARAT SINGH, BIRENDRA BAHADUR SINGH and SATYENDRA SINGH

Chemical Laboratories, University of Allahabad, Allahabad-211 002

Manuscript received 24 September 1979, accepted 30 December 1979

The kinetics of hexacyanoferrate(III) ion oxidation of N-methylmorpholine in aqueous alkaline medium at constant ionic strength has been studied at four temperatures. The data show that the reaction follows first order kinetics with respect to each of the hexacyanoferrate(III) ion, N-methylmorpholine and hydroxide ion. The energy of activation and entropy of activation have been calculated to be 13.84 KCal/mole and -23.81 e.u. respectively. The net rate of oxidation of N-methylmorpholine as measured by the consumption of hexacyanoferrate(III) ion, is given by

$$-\frac{d[Fe(CN)_6^{-3}]}{dt} = \frac{k_1 k_2}{k_{-1}[H_2O]}[M][OH^-][Fe(CN)_6^{-3}]$$

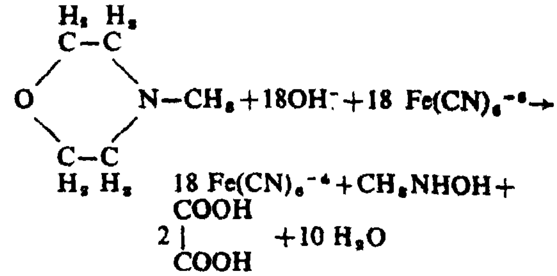
THE authors[1-2] have suggested that alkaline hexacyanoferrate(III) ion simply acts as an electron abstracting reagent in redox reactions. However, Speakman and Waters[3] have suggested a different paths of oxidation of aldehydes, ketones and nitroparaffins. Singh and coworkers[4-6] while discussing the oxidations of formaldehyde, acetone and ethyl methyl ketone have suggested that the oxidation takes place via an electron transfer process resulting in the formation of a free radical intermediate. The present study aims at finding out a suitable mechanism for the oxidation of N-methylmorpholine by alkaline hexacyanoferrate(III) ions on the basis of kinetic results.

Materials and Method :

The sample of N-methylmorpholine (Fluka Grade) was used without any further purification. Potassium hexacyanoferrate(III), ferrous ammonium sulphate and sodium hydroxide used were S. Merck (G. R.) grade. Other chemicals used were sodium chloride B.D.H. (A.R.), Ferroin E. Merck and methyl alcohol (B.D.H.). The rate of oxidation was determined titrimetrically by usual method[4].

Stoichiometry :

The stoichiometry of the reaction was obtained by taking excess of potassium hexacyanoferrate(III) over N-methylmorpholine to interact 1.2 *M* NaOH at 35°. The results showed that eighteen moles of potassium hexacyanoferrate(III) were consumed per mole of N-methylmorpholine and accordingly the stoichiometry may be represented as follows :



Results and Discussion

The kinetic data for the oxidation of N-methyl morpholine by aqueous alkaline hexacyanoferrate(III) ion at constant ionic strength and at four temperatures are given in Tables 1-2. The constant value of pseudo first order rate constant k_1 (Table 1) shows that the reaction follows first order kinetics with respect to hexacyanoferrate-(III) ion. This was further confirmed by the standard first order plot between log (a-x) and time (a-x)=-remaining concentration of hexacyanoferrate-(III) ion). Pseudo first order rate constants obtained at different concentrations of both N-methylmorpholine and hydroxide ion were directly proportional to the concentrations of N-methylmorpholine and hydroxide ion respectively showing thereby first order dependence of the reaction on each N-methylmorpholine and hydroxide ion. This was also confirmed by constant value of second order rate constant k_2 given in the last column of the Table 1. Second order rate constants were calculated for N-methylmorpholine and hydroxide ion by dividing k_1 values with the concentrations of N-methylmorpholine and hydroxide ion respectively. It was observed that the ionic strength of the medium has a positive effect on the rate of the reaction. The effect of dielectric constant on reaction rate was also

TABLE 1—EFFECT OF VARYING REACTANTS ON RATE OF REACTION

Ionic Strength (μ) = 1.512*M*

Temp. °C	$[K_3Fe(CN)_6] \times 10^3$ M	[N-Methyl-morpholine × 10] M	$[OH^-] \times 10$ M	$k_1 \times 10^3 min^{-1}$ Calculated	$k_1 \times 10^3 min^{-1}$ Graphical	$k_2 \times 10^2$ l mole^{-1}min^{-1}
40	1.00	1.00	12.0	10.74	10.59	-
40	1.33	1.00	12.0	9.87	9.58	-
40	1.67	1.00	12.0	9.23	8.64	-
40	2.00	1.00	12.0	9.15	8.69	-
40	2.50	1.00	12.0	8.52	8.23	-
40	3.33	1.00	12.0	8.78	8.26	-
40	4.00	1.00	12.0	8.56	8.37	-
40	5.00	1.00	12.0	8.58	8.15	-
30	2.00	1.00	12.0	3.95	-	-
35	2.00	1.00	12.0	6.03	-	-
45	2.00	1.00	12.0	12.44	-	-
40	2.00	0.50	12.0	5.31	-	11.05
40	2.00	0.67	12.0	6.35	-	9.52
40	2.00	0.80	12.0	7.31	-	9.14
40	2.00	1.00	12.0	9.15	-	9.15
40	2.00	1.33	12.0	11.15	-	8.38
40	2.00	1.50	12.0	12.60	-	8.40
40	2.00	2.00	12.0	16.13	-	8.01
40*	2.00	1.00	2.50	2.90	-	1.16
40*	2.00	1.00	4.00	4.40	-	1.10
40*	2.00	1.00	5.00	5.61	-	1.12
40*	2.00	1.00	6.00	6.92	-	1.15
40*	2.00	1.00	8.00	8.89	-	1.11
40*	2.00	1.00	10.00	11.40	-	1.14

*$\mu = 2.012 \times 10^{-1} M$

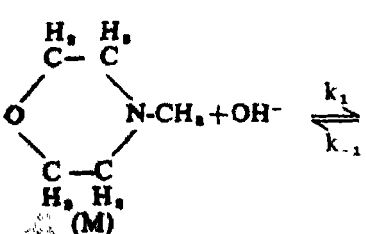
studied by employing different concentrations of methanol-water mixture and it was observed that an increase in methanol concentration has a retarding effect on the reaction rate (Table 2).

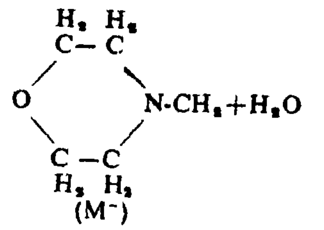
TABLE 2—EFFECT OF DIELECTRIC CONSTANT (D)

Vol % Methanol	D	$k_1 \times 10^3$
0	78.50	9.15
5	72.76	6.17
10	70.68	4.90
15	68.62	4.18
20	66.52	3.23
25	64.38	2.51

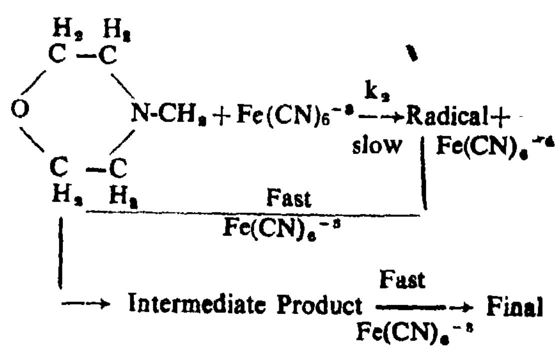
$[K_3Fe(CN)_6] = 2.00 \times 10^{-3} M$, [N-Methylmorpholine] = $1.00 \times 10^{-1} M$, [NaOH] = $1.20M$, $\mu = 1.512 \times 10^{-1} M$ and Temp. 40° C

In the light of above observations, the probable mechanism of oxidation may be considered as follows :





... (i)



Products...(ii)

The rate of oxidation of N-methylmorpholine can be expressed by rate of disappearance of hexacyanoferrate(III) ion concentration as shown in step (ii) i.e.,

$$-\frac{d[Fe(CN)_6^{-3}]}{dt} = k_2 [Fe(CN)_6^{-3}][M^-] \quad ...(I)$$

The net rate of oxidation of morpholine thus can be

obtained on substituting the value of $[M^-]$ from step (i) in equation (I) and is given as

$$-\frac{d[Fe(CN)_6^{-3}]}{dt} = \frac{k_1 k_2 [M][OH^-][Fe(CN)_6^{-3}]}{k_{-1}[H_2O]+[k_2][Fe(CN)_6^{-3}]} \quad \text{... (II)}$$

where M is the substrate.

If the value of k_2 is of low magnitude such that $k_2[Fe(CN)_6^{-3}] \ll k_{-1}[H_2O]$ exists, the equation (II) becomes

$$-\frac{d[Fe(CN)_6^{-3}]}{dt} = \frac{k_1 k_2}{k_{-1}[H_2O]}[M][OH^-][Fe(CN)_6^{-3}] \quad \text{... (III)}$$

The observed first order dependence of the reaction on each hexacyanoferrate(III) ion, N-methylmorpholine and hydroxide ion concentration is obvious from the rate equation (III). The rate determining step (ii) involves interaction between two anions and in such reactions a positive salt effect is expected which is in agreement with our observations. This was further confirmed by the negative slope[6] of the plot of log k_1 versus 1/D where D is dielectric constant of the medium.

The free radical formed is probably fast oxidised with alkaline hexacyanoferrate(III) ion to intermediate products which undergo further oxidation to oxalic acid and the other products. In most of the oxidation reactions hexacyanoferrate(III) ion resembles the copper(II) which involves free radical[7-9] formation and rapidly oxidises it. The Fe(III)-Fe(II) system, which has higher redox potential than Cu(II)-Cu(I), substantiates better possibility of the rapid oxidation of the free radicals with hexacyanoferrate(III) ion in the alkaline medium and the rapid oxidation of the radicals might completely mask the polymerization test. Some times vinyl compounds themselves are oxidised under the experimental conditions used and the test for the free radicals[10] fails. Moreover, no spectrophotometric test for complex formation was observed. Oxalic acid was identified by chromatographic technique.

The values of energy of activation and entropy of activation are 13.84 K Cal/mole and -23.81 e.u. respectively. The high negative value of entropy also supports the proposed mechanism involving two negatively charged ions.

Acknowledgement

One of the authors (S.S.) is thankful to U. G.C., Government of India, New Delhi for granting U.G.C. Teacher Fellowship.

References

1. I. R. Wilson, *Rev. Pure Appl. Chem.*, 1966, **16**, 103.
2. B. S. Thyagratan, *Chem. Rev.*, 1958, **58**, 459.
3. P. T. Speakman and W.A. Waters, *J. Chem. Soc.*, 1955, 40.
4. V. N. Singh, M. C. Gangwar, B. B. L. Saxena and M. P. Singh, *Canad. J. Chem.*, 1969. **47**, 1051.
5. V. N. Singh, M. P. Singh and B. B. L. Saxena, *Indian J. Chem.*, 1970, **8**, 529.
6. E. S. Amis and V. K. Lamer, *J. Amer. Chem. Soc.*, 1939, **61**, 905.
7. M. P. Singh and S. Ghosh, *Z. Phys. Chem.*, 1955, **204**, 1 ; 1957, **207**, 187, 198.
8. K. B. Wiberg and W. G. Nigh, *J. Amer. Chem. Soc.*, 1965, **87**, 3849.
9. J. K. Kochi, B. M. Grabill and M. Kwiz, *J. Amer. Chem. Soc.*, 1964, **86**, 5257.
10. V. N. Singh, M. P. Singh and B. B. L. Saxena, *Indian J. Chem.*, 1970, **8**, 529.

J. Indian Chem. Soc.,
Vol. LVII, March 1980, pp. 318-320

Kinetics and Mechanism of Oxidation of Dulcitol by Chloramine-T

S. P. MADNAWAT, VEENA SINGH and D. R. SINGH

Chemical Laboratories, R.B.S. College, Agra, India

Manuscript received 23 July 1979, accepted 29 December 1979

Kinetics of oxidation of dulcitol by chloramine-T in alkaline media has been investigated. A brief initial induction period has been observed after which the reaction shows a first order dependence each in [chloramine-T], [dulcitol] and [OH⁻]. The effect of added neutral salts on the reaction rate is negligible. Energy of activation is observed to be 33.3 Kcal/mole for the reaction. A plausible mechanism consistent to the experimental data has been proposed.

THE kinetics of oxidation of several alcohols by chloramine-T in acidic media has been investigated by Mushran *et al*[1-3]. Natarajan and Thiagarajan[4] have also studied the oxidation of secondary alcohols in acidic media. Recently Mahadevappa and Naidu have also studied the chloraminometric oxidation of allyl alcohol[5,6] and cinnamyl alcohol[7]. The oxidation of polyhydric alcohols by chloramine-T has not been studied so far. In this communication, the study of kinetics of oxidation of dulcitol in alkaline media is made. The progress of reaction in neutral or acidic media is found too slow to be studied kinetically.

Experimental

Aqueous solution of dulcitol (E. Merck) was prepared. Stock solutions of chloramine-T (E.Merck) and sodium hydroxide (A.R.) were prepared. The solutions were stored in black coated bottles to prevent photochemical influences[8]. All other chemicals viz. KNO_3, K_2SO_4, $NaNO_3$ and Na_2SO_4 were of analytical grade. Double-distilled water was always used for the prepration and dilution of the solutions throughout the course of reaction.

Reactants were brought to thermostatic temperature ($\pm 0.1°$) and allowed the reaction mixture to equilibrate for 30 minutes after which an appropriate amount of chloramine-T was added to initiate the reaction. The kinetics was followed by estimating chloramine-T iodometrically in aliquot portion of the reaction mixture withdrawn after definite time intervals.

Results

(*a*) *Stoichiometry* :

Reaction mixtures containing excess of chloramine-T over dulcitol were allowed to equilibrate at 40° in respective sodium hydroxide concentration. The results showed that one mole of dulcitol was oxidised by three moles of chloramine-T forming galactonic acid which was examined by positive spot test. Thus the stoichiometric equation for the reaction may be represented as :

$$3CH_3C_6H_4SO_2N.NaCl + C_6H_{14}O_6 + OH^- + H_2O \rightarrow 3CH_3C_6H_4SO_2NH_2 + C_6H_{11}O_7^- + 2NaCl + NaClO$$

(*b*) *Chloramine-T dependence* :

The oxidation of dulcitol by chloramine-T was investigated in highly alkaline media. It was observed that the reaction shows a brief initial induction period after which first order dependence on chloramine-T was observed. Pseudo first order rate constants (k_1) were calculated from the slopes of log [chloramine-T]—time plots of several initial concentrations of chloramine-T. A fairly constant value $0.58 \pm 0.03 \times 10^{-2}$ min^{-1} was obtained.

(*c*) *[Dulcitol] dependence* :

The dependence with respect to dulcitol was determined by carrying out the kinetic runs with its different concentrations and keeping the concentrations of other reactants constant. A linear increase in first order rate constants calculated from $k_2 = k_1/$[dulcitol] gave concordant values establishing a first order dependence in dulcitol (Table 1).

TABLE 1 – EFFECT OF DULCITOL CONCENTRATION ON REACTION RATE

[Chloramine-T] = $1.0 \times 10^{-3}M$, [NaOH] = $6.0 \times 10^{-3}M$, temp. = 35°C.

[Dulcitol] × $10^3 M$	$k_1 \times 10^2$ min^{-1}	k_1/[dulcitol] min^{-1} mole^{-1}
0.5	0.30	0.60
0.6	0.37	0.61
0.7	0.42	0.60
0.8	0.47	0.59
0.9	0.53	0.59
1.0	0.57	0.57
1.1	0.62	0.56
1.2	0.70	0.58

(*d*) *[NaOH] dependence* :

The rate of oxidation of dulcitol by chloramine-T was found to be enough sensitive to the change in OH^- ion concentration. Influence of NaOH concentration variation on reaction rate was studied by taking fixed concentrations of oxidant and substrate and varying the concentration of NaOH.

First order dependence in NaOH was established by getting concordant values of k_1 [NaOH] for a wide range of NaOH concentration (Table 2).

TABLE 2—EFFECT OF [NaOH] ON REACTION RATE

[Chloramine-T] = $1.0 \times 10^{-3}M$, [Dulcitol] = $1.0 \times 10^{-2}M$, temp. = 35°C

[NaOH] × 10^3M	$k_1 \times 10^3$ min^{-1}	k_1/[NaOH] min^{-1} mole^{-1}
4.0	0.35	0.88
6.0	0.57	0.95
8.0	0.74	0.92
10.0	0.90	0.90
12.0	1.07	0.89
14.0	1.26	0.90
16.0	1.47	0.92
18.0	1.66	0.92

(e) *Rate dependence on ionic strength* :

The effect of added neutral salts was found to be negligible on the reaction rate (Table 3).

TABLE 3—EFFECT OF IONIC STRENGTH

[Chloramine-T] = $1.0 \times 10^{-3}M$, [Dulcitol] = $1.0 \times 10^{-2}M$, [NaOH] = $6.0 \times 10^{-3}M$, temp. = 35°C.

[Salt] × 10^3M	$k_1 \times 10^3$ min^{-1}			
	KNO_3	K_2SO_4	$NaNO_3$	Na_2SO_4
2.0	0.59	0.54	0.53	0.58
4.0	0.57	0.55	0.54	0.53
6.0	0.55	0.52	0.55	0.53

(f) *Temperature dependence* :

Kinetic runs were carried out at four different temperatures to calculate the energy of activation for the reaction. The pseudo first order rate constants at different temperatures are summarised in Table 4.

TABLE 4—EFFECT OF TEMPERATURE

[Chloramine-T] = $1.0 \times 10^{-3}M$, [Dulcitol] = $1.0 \times 10^{-2}M$, [NaOH] = $6.0 \times 10^{-3}M$.

Temp. °C	32.5	35	37.5	40
$k_1 \times 10^3$ min^{-1}	0.35	0.57	0.80	1.3

The energy of activation was calculated from the slope of Arrhenius plot which was found to be 33.3 Kcal/mole.

Discussion

Dulcitol is rapidly converted into galactose by alkaline chloramine-T. Hence the kinetics of oxidation of dulcitol is related to the kinetics of oxidation of galactose. The experimental findings reveal that the reaction followed a first order dependence each in [chloramine-T], [dulcitol] and [NaOH]. The effect of added neutral salts was found to be insignificant which leads to the conclusion that the reaction takes place between neutral molecules or between an ion and a neutral molecule. The following mechanism has been proposed which has been found in consonance with the experimental results.

Aqueous solution of chloramine-T hydrolyses to *p*-toluene sulphochloramide and sodium hydroxide.

$$CH_3C_6H_4SO_2N\,NaCl + H_2O \rightleftharpoons CH_3C_6H_4SO_2N.HCl + NaOH \quad ...(1)$$

Under experimental condition (at high alkali concentration) equilibrium almost lies towards left i.e. almost all the chloramine-T is in unhydrolyesed form which itself should be an effective species. Direct dependence on [NaOH] also supports this fact.

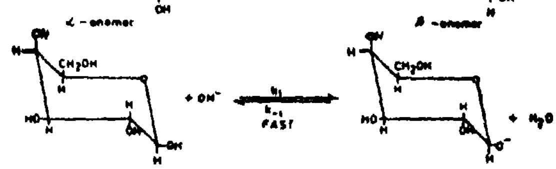
Dulcital is fast converted into galactose.

$$\text{Dulcitol} + \text{Chloramine-T} \xrightarrow{\text{fast}} \text{Galactose} \quad ...(2)$$

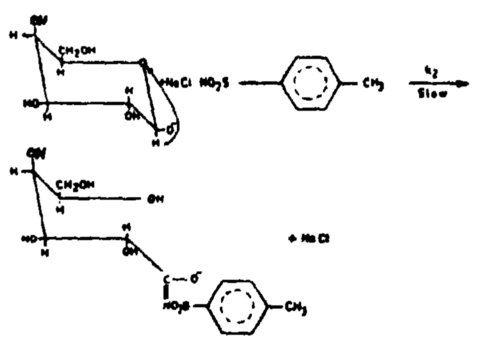
Galactose exists in two anomeric forms which are in equilibrium in aqueous solution. The conformations of these are



.. (3)



...(4)



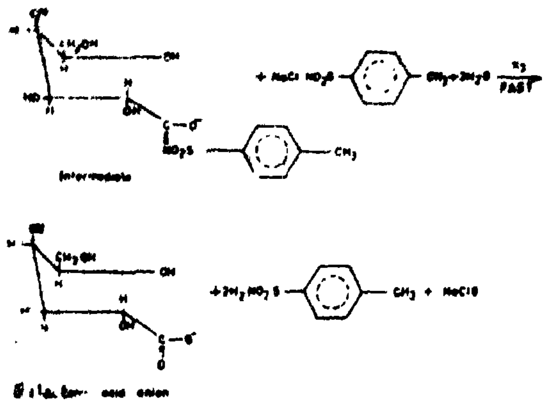
...(5)

Intermediate

β-anomer is more reactive and the anion of this β-anomer exists in alkaline aqueous medium[9-11].

This anion reacts with chloramine-T (oxidising species) itself in a slow step to form an intermediate which further interacts in a fast step with chloramine-T to generate products. Equations are as under :

Applying steady galactonic acid anion state



...(6)

assumption to the intermediates and assuming that water is in large excess and k_{-1} $[H_2O] \gg k_3$ [chloramine-T] the rate of disappearance of chloramine-T is given by

$$\frac{-d}{dt}[\text{chloramine-T}] = k_1 [\text{chloramine-T}] [\text{galactose}] [OH^-]$$

$$\text{where } k_1 = \frac{2k_1k_3}{k_{-1}[H_2O]}$$

Since dulcitol is converted into an equivalent amount of galactose in a fast step.

$$[\text{dulcitol}] = [\text{galactose}]$$

Thus the rate law is

$$\frac{-d}{dt}[\text{chloramine-T}] = k_1 [\text{chloramine-T}] [\text{dulcitol}] [OH^-]$$

Acknowledgement

S.P.M. is highly thankful to CSIR for an award of Junior Research Fellowship. The authors are also indebted to Dr. R.S. Parihar and Dr. O.P. Singh, Department of Chemistry, R.B.S. College, Agra for their kind help and suggestions.

References

1. S. P. Mushran, R. M. Mehrotra and R. Sanehi, *J. Indian Chem. Soc.*, 1974, **51**, 594.
2. S. P. Mushran, R. M. Mehrotra and R. Sanehi, *Proc. Natl. Acad. Sci., India* (A), 1973, 43, 105.
3. S. P. Mushran, R. M. Mehrotra and A. Kumar, *Bull. Acad. Pol. Sci.*, 1976, **24**, 181.
4. M. M. Natarajan and V. Thiagarajan, *J. Chem. Soc. Perkin II*, 1975, 1590.
5. D. S. Mahadevappa and H. M. K. Naidu, *Aust. J. Chem.*, 1974, **27**, 1203.
6. D. S. Mahadevappa and H. M. K. Naidu, *Aust. J. Chem.*, 1975, **28**, 899.
7. D. S. Mahadevappa and H. M. K. Naidu, *Indian J. Chem. Sect.* A, 1976, **14**, 808.
8. W. Poethke and F. Wolf, *Z. anorg. allegem Chem.*, 1952, **268**, 244.
9. I. R. L. Barker, W. G. Overend and C. W. Ress, *Chem. Ind.*, 1960, 1297.
10. B. Perlmutter-Hayman and A. Persky, *J. Amer. Chem. Soc.*, 1960, **82**, 276.
11. M. C. Agarwal and S. P. Mushran, *J. Chem. Soc., Perkin II*, 1973, 762.

J. Indian Chem. Soc.,
Vol. LVII, March 1980, pp. 321-324

Study on the Thermal Decomposition of Ammonium Nitrate Using Mass Spectrometric Technique

S. K. ADHYA, S. K. MUKHERJEE and B. K. BANERJEE

Research & Development, The Fertilizer (P & D) India Ltd., P.O. Sindri-828 122, Dhanbad (Bihar), India

Manuscript received 6 September 1979, accepted 30 December 1979

Thermal decomposition of ammonium nitrate in the temperature range 40 to 200° under reduced pressure (10^{-6} – 10^{-4} torr) with continuous removal of the evolved gases has been carried out with the help of a mass spectrometer. The analysis of evolved gases at different stages of temperature reveals that the decomposition process is strongly temperature dependent and follows three distinct paths in the three different temperature ranges which are briefly represented as follows :

$$\text{(A)}\quad NH_4NO_3 \xrightarrow{40\ \text{to}\ 140^\circ C} NH_3 + HNO_3$$
$$HNO_3 \longrightarrow NO_2 + H_2O + O_2 + NO$$
$$\text{(B)}\quad NH_4NO_3 \xrightarrow{150-170^\circ C} N_2O + H_2O$$
$$\text{(C)}\quad NH_4NO_3 \xrightarrow{170-200^\circ C} NO + H_2O$$

Measurements of ion intensity ratios against temperatures supports these findings.

AMMONIUM nitrate exhibits a tendency to decompose on keeping due to thermal effects and interaction with the environment. This encouraged numerous workers to study its thermal decomposition mechanism[1,6,9,10,16,20,22,28,30]. Several attempts have also been made to determine the composition of evolved gas mixture[9,15,25,28], effects of various additives[3,18,22] and determination of rate constants[2,7,9,14,25,26,30]. Various physical techniques like mass spectrometry[8,29] and gas chrmotography[4] have also been applied to assist such studies from time to time.

In 1954, Feick and Hainer[11] suggested that at 170°, NH_3 and HNO_3 were formed first followed by the formation of N_2O and H_2O at 290°. Later on in 1968, Heinrich[13] contradicted Feick,s findings and reported that the initial formation was N_2O and H_2O, whereas NH_3 and HNO_3 were formed at the second stage. Party *et al.*[20] detected hydrazine in the reaction products between NH_3 and NO_2 upto 100° whereas Guiochon[12] found the intermediate formation of NH_2NO_2 species in the above decomposition process. In early seventies Manclis[17] critically reviewed its decomposition process. Later on in 1975 Biskupski and Kotaczkowski[5] did further work in the line.

In the present investigation the decomposition of ammonium nitrate has been studied inside the mass spectrometer source chamber where high vacuum (10^{-6} torr) is maintained constantly. This technique facilitates the immediate detection of any intermediate or transient species formed as the possibility of gas phase interaction is automatically minimized and will help in understanding the decomposition mechanism of ammonium nitrate.

Experimental

Ammonium nitrate sample used in this experiment was of AnalaR variety. Aqueous solution of the sample was taken in the glass capillary sample tube and dried in a desiccator. The dried sample was then introduced in the mass spectrometer through the solid introduction probe. The spectra were recorded from 40 to 140° with 20° interval and at 170° and 200° also, setting the mass scanning range from m/e 12 to 100. High resolution, high speed analysis was carried out for the detailed analysis of individual mass peaks at m/e17,18,30, 44, 46 and 63.

The ion intensity ratio values are shown in Table 1.

The apparatus used in this study was a double focussing double beam MS30DB mass spectrometer, supplied by M/s.AEI England, operated under the following conditions :

Nature of Ionization	:	Electron Impact
Electron volts	:	70 e. v.
Electron current	:	300μA
Accelerating Voltage	:	4 KV
Scan Speed	:	30 sec/Dec
Resolution	:	1000 & 3000
Sensitivity	:	6.0
Source Temperature	:	60-220°
Reference Material	:	Perfluoro Kerosine.
Recording	:	U. V. Oscillographic

TABLE 1—PEAK INTENSITY RATIOS OF DIFFERENT IONS OF NH_4NO_3 AT VARIOUS TEMPERATURES

TEMPERATURE	INTENSITY RATIO OF				
	$(NO^+)30/46(NO_2^+)$	$(NH_3^+)17/63(HNO_3^+)$	$(N_2O^+)17/63(HNO_3^+)$	$(NO^+)44/63(HNO_3^+)$	$(N_2O^+)44/46(NO_2^+)$
40	0.637	—	—	—	—
60	0.617	40.0	0.1	3.2	0.144
80	0.627	40.9	0.342	6.0	0.141
100	0.611	45.0	0.428	6.0	0.166
120	0.622	-	0.416	6.25	0.196
140	0.603	41.66	3.0	20.0	0.190
170	8.0	—	2.909	—	40.0
200	13.33	—	0.555	—	8.33

Results and Discussion

The absence of parent peak (m/e 80) in the temperature range 40-200° indicates the unstability of ammonium nitrate both thermally and under electron impact. Among the few peaks observed in the spectra at 40°, m/e 17 is found to be double natured and shows the presence of both NH_3^+ and OH^+ ions in which the intensity of NH_3^+ ion is more. The peak at m/e 30 and m/e 46 are confirmed to be due to NO^+ and NO_2^+ respectively which are formed in the following way :

$$NH_4NO_3 \longrightarrow HNO_3+NH_3 \quad \ldots \text{(A)}$$
$$4HNO_3 \longrightarrow 2H_2O+4NO_2+O_2 \quad \ldots (A_1)$$
$$4NO_2 \longrightarrow NO + 2O_2 \quad \ldots (A_2)$$

The formation of NO^+ ion may also be due to fragmentation of NO_2^+ under electron impact. The peak due to HNO_3^+ (m/e 63) appears at 60° and persists prominently upto 140°. Upto this temperature range it is found that the variation in the ratios of NH_3^+/HNO_3^+ is nearly constant (Fig. 1) which clearly indicates that NH_3^+ and HNO_3 formation is the product of the same reaction and is designated as the first path (Path A) of thermal decomposition of NH_4NO_3 which is also reported earlier[21,23]. The weak intensity of m/e 63 peak with respect to NH_3^+ peak reveals the relative unstability of HNO_3^+ under the experimental condition. After 140° the peak at m/e 17 is due to OH^+ ion only as confirmed from its singlet nature.

The spectra in the temperature region 170-200° shows the presence of intense peaks of H_2O^+ m/e 18, OH^+ at m/e 17 and not due to NH_3^+ as is evident from its singlet nature and a peak at m/e 44 due to N_2O^+ ion as confirmed by fast scanning and high resolution settings (Fig. 2).

The ion intensity ratio of (N_2O^+/H_2O^+) at different temperatures (Fig. 1) is found to be constant in the temperature range 140 to 170° which confirms that these fragments are the results of the following reaction

$$NH_4NO_3 \longrightarrow N_2O + H_2O \quad \ldots \text{(B)}$$

which is considered as the second decomposition path, (path B). The spectra at 200° shows major peaks at m/e 18 due to H_2O^+ (base peak), m/e 30 due to NO^+ and an abrupt reduction in the intensity of m/e 44 peak. It is therefore, concluded that at higher temperature NH_4NO_3 produces NO and H_2O as the ultimate product.

$$NH_4NO_3 \xrightarrow{\text{at } 200°C} NO + H_2O \quad \ldots \text{(C)}$$

A weak but very persistent peak at m/e 64 which is confirmed to be due to NH_4NO_2 ion is found to be present from 60 to 200° which has probably formed due to electronic fragmentation of NH_4NO_3. According to P. Ray *et al.*[19] NH_4NO_2 once formed can be sublimed undecomposed under reduced pressure upto 60°. As the vacuum order in the present experimental condition is very high (approx 8×10^{-6} to 9×10^{-7} torr) it is very much probable that NH_4NO_2 formed remained undecomposed even upto 200°.

A better understanding of the results and important features of the different species formed is obtained by plotting the ion intensity ratios against temperature. As stated earlier the ratio of NH_3^+/HNO_3^+ (Fig. 1a) is practically constant suggesting their interrelated formation. In a similar way the ratio of N_2O^+/H_2O^+ (Fig. 1b) is constant in the

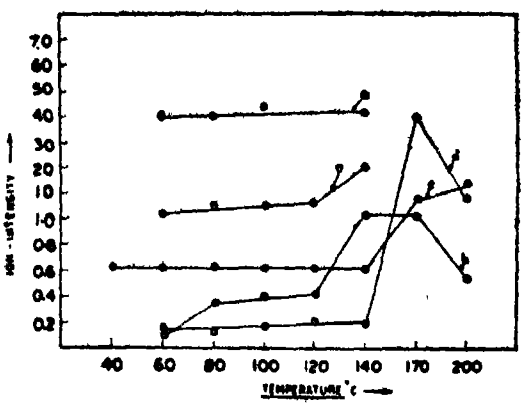


Fig. 1. Relative ion intensity vs temperature curves of (a) NH_3^+/HNO_3^+, (b) N_2O^+/H_2O^+, (c) N_2O^+/HNO_3^+, (d) N_2O^+/NO_2^+, (e) NO^+/NO_2^+.

temperature range 140 to 170° indicating that reaction (B) takes place in this range. A sudden fall in

the ratio value of N_2O^+/H_2O^+ above 170° and upto 200° shows that after 170° either N_2O formation decreases or H_2O formation increases. The spectra gives a clear indication that with increase of temperature N_2O formation decreases. This is further supported by an increase in the ratio value of NO^+/NO_2^+ after 170° and a sudden fall in the ratio of N_2O^+/NO_2^+ after 170° (Fig. 1d). Below 140°, the lower portion of the ratio plot of N_2O^+/H_2O^+ (Fig. 1b) indicates that initially either some moisture was present in the sample, or water is formed as a result of chemical interaction amongst the decomposition products of NH_4NO_3 as indicated below.

$$NH_4NO_3 \longrightarrow NH_3 + HNO_3 \quad \ldots \quad (D)$$
$$5NH_3 + 3HNO_3 \longrightarrow 9H_2O + 4NO_2$$

which is slowly lost with the further increase of temperature and ceases after 120°.

The constant ratio values of NO^+/NO_2^+ (Fig. 1c) in the temperature range 40-140° show that NO^+ is formed[2] totally from NO_2^+ by electronic impact. Above 140° a steep rise in the curve indicates that NO^+ is also formed from NH_4NO_3 by thermal decomposition. The ratio value of N_2O^+/NO_2^+ (Fig. 2) is approximately constant upto 140° having a maximum at 170°. confirming its maximum formation there. After 170° N_2O^+/NO_2^+ ratio again falls down showing reduction in N_2O^+ formation at higher temperatures.

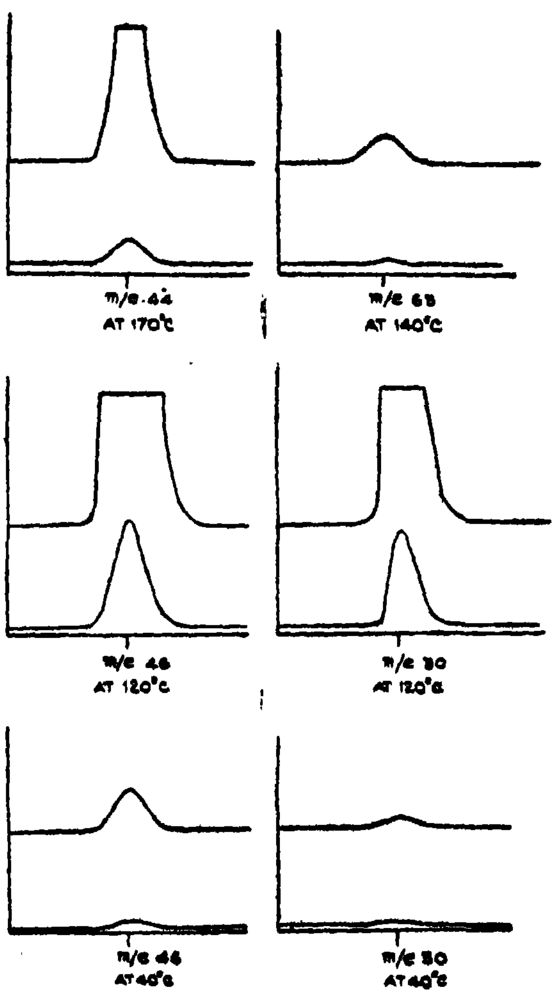


Fig. 2. High speed and high resolution mass spectra of M/E 63, 46, 44, 30 at different temperatures.

The experimental results show that the thermal decomposition of NH_4NO_3 is strongly temperature dependent. With variation of temperature it follows three different decomposition routes namely (A), (B) and (C). The reactions (A) and (B) occur simultaneously with ceasing of reaction (A) after certain temperature, where reaction (B) become more prominent. At still higher temperatures the decomposition follows path (C). The variation in the reaction temperatures as observed is attributed to be due to the high vacuum prevailed during the experiment.

Acknowledgement

The authors are thankful to Prof. T. C. Rao, Head of the Department of Chemistry and Mineralogy, Indian School of Mines, Dhanbad for helpful suggestions and Dr. P. C. Srivastava, for encouragement in the work.

References

1. K. S. Barclay and J. M. Crewe, *J. Appl. Chem. London*, 1967, **17**, 21.
2. K. S. Barclay, J. M. Crewe and E. J. Smith, *Nature, London*, 1963, **198**, 1054.
3. C. C. Berland and E. D. Schall, *J. Assoc. Office. Agr. Chemists*, 1959, **42**, 579.
4. D. Bennett, *J. Appl. Chem. Biotechnol*, 1972, **22**, 973.
5. A. Biskupski, A. Kotaczkowski and J. Schroeder, Therm. Anal. Vol. 3, p. 577. Ed. I. Bezas. Akademiai, Kiado, Budapest, 1973.
6. G. N. Buspalov, L. B. Filatova and A. A. Shidlovskii, *Zh. Fiz. Khim.*, 1968, **10**, 2623.
7. M. A. Coock and M. T. Abegg, *Ind. Engg. Chem.*, 1976, **48**, 1090.
8. S. L. Dobychin and V. M. Smirnov, *Zh. Prikl. Khim.*, 1963, **36**, 215.
9. T. L. Davis and A. J. J. Abrams, *J. Amer. Chem. Soc.*, 1925, **47**, 1043.
10. L. Friedman and J. Bigelstein *J. Chem. Phys.*, 1950, **18**, 1325.
11. Geo Feick and M. R. Hainer, *Nature*, 1954, **173**, 1188.
12. G. Guiochon. *Ann. Chim.*, 1960, **13**, 5, 295.
13. J. H. Heinrich *Explosives-toffe*, 1964, **12**, 23.
14. A. G. Keenan, and B. Dimitriades, *Trans. Faraday Soc.*, 1961, **57**, 1019.
15. W. Z. Kretzschmar, *Anorg. Allg. Chem.*, 1934, **2**, 17.

16. J. T. KUMMER, *J. Amer. Chem. Soc.*, 1947, 69, 2559.
17. G. B. MANCLIS, YU. I. RUBSTEOV and A. G. RAETSKII., *Fiz. Goreniya Vzryva*, 1970, 6, 3.
18. G. H. MANADAY and G. BURNET., *J. Agr. Food Chem.*, 1958, 16, 137.
19. J. W. MELLOR, A Comprehensive Treatise on Inorganic and Thertetical Chemistry, Vol. VIII, 471, Longmans Green and Co.
20. M. Patry, R. GARLET and S. PUPKO, *Compt. Rend.*. 1947, 225, 941.
21. W. A. ROSSER, S. H. INAMI and H. WISE., *J. Phys. Chem.* Ithaca, 1963, 67, 1753.
22. B. YUN ROZMAN and L. I. BORODKINA., *Zh. Prikl. Khim.*. 1959, 32, 271.
23. B. YU. ROZMAN, *Zh. Prikl. Khim.*, 1960, 33, 1052.
24. J. C. REISCH, and G. BURNET, *J. Agri. Food Chem.* 1965, 13, 311.
25. A. J. B. ROBERTSON, *J. Soc. Chem. Ind. Lond.*, 1948, 67, 221.
26. M. S. SHAH and R. M. OZA, *J. Chem. Soc.*, 1939, 725.
27. H. L. SAUNDERS, *J. Chem. Soc.*, 1922, 121, 698.
28. J. SOJKA, *Chemicky, Prum.*, 1956, 6, 45.
29. T. SHIRAI, and Nishikawa, *Sci. Papers. Coll. Gen. Edu. Univ. Tokyo*, 1959, 9, 17.
30. B. J. WOOD and H. WISE, *J. Chem. Phys.*, 1955, 23 693.

J. Indian Chem. Soc.,
Vol. LVII, March 1980, pp. 325-329

Determination of Solubility Product of Silver Bromide at a Number of Temperatures

A. C. JHA and B. PRASAD

Department of Chemistry, Patna University, Patna

Manuscript received 27 October 1978, accepted 9 February 1980

Solubility product of silver bromide has been determined from 15° to 55° at 10° intervals from e.m.f. measurements of a series of cells of the type given below :

$$Ag \left| AgBr \begin{matrix} KBr(x)c \\ KNO_3(1-x)c \end{matrix} \right| KNO_3\, c \left| \begin{matrix} AgNO_3(x)c \\ KNO_3(1-x)c \end{matrix} \; AgBr \right| \; Ag$$

ΔH°, ΔG° and ΔS° of the reaction $AgBr = Ag^+ + Br^-$ have also been cacualated.

EARLIER determinations[1-5] of solubility product of silver bromide differed by more than 20% in some cases. Recently Gledhill and Malan[6] determined the solubility product by measuring conductance. Owen and Brinkley[7] calculated the same from E° values of Ag/Ag^+ and $Ag/AgBr, Br^-$ electrodes. At some temperatures the difference in solubility product determined by the two sets of authors comes to 10%. So it was decided to undertake this study with the help of cells $Ag \mid AgBr \begin{matrix} KBr(x)c \\ KNO_3(1\text{-}x)c \end{matrix} \mid KNO_3c \mid \begin{matrix} AgNO_3(x)c \\ KNO_3(1\text{-}x)c \end{matrix}$ AgBr | Ag. These cells were similar to those studied by Owen[8] in the determination of solubility product of silver chloride and these cells were also studied by Gledhill and Malan[9] at 25°. Our method of calculation is slightly different from that of Owans or Gledhill and Malan.

Experimental

All solutions were prepared in molarity in doubly distilled water from G.R. quality salts at the experimental temperature. The concentrations of the stock solutions of silver nitrate and potassium bromide were checked volumetrically[10]. The experimental solutions were deoxygenated by passing presaturated nitrogen gas. Thermal electrolytic silver-silver bromide electrodes used in the experiments were prepared following the method of Harned and Douglas[11], the only difference being that the platinum spiral was coated directly with silver oxide paste instead of electroplating it first with silver and then coating with silver oxide. The electrode vessels, bridges and setting up the cells were similar to that described earlier[12]. Temperature control was within ±0.05°. Tinsley Vernier Potentiometer was used. All the cells were studied in duplicate and the duplicates generally agreed within 0.1 mV., though in a very few cases difference went up to 0.15 mV. The mean values of E (in absolute volts) are given in Tables 1-5. The values of 'A' in molarity scale have been taken from the work of Manov, Bates, Hamer and Acree[13].

Discussion

At every temperature five series of experiments were performed and every series had five sets of experiments. In every series 'c' was fixed and 'x' was varied. E.M.F. of a cell of any particular series is given by

$$E = \frac{RT}{F} \ln \frac{a_1}{a_2} + \text{l.j.p.} = \frac{RT}{F} \ln \frac{a_1 a_3}{K_{sp}} + \text{l.j.p.} \quad \dots (1)$$

where a_1 indicates activity of silver ion in the mixture of silver nitrate and potassium nitrate, a_2 and a_3 indicate activity of silver ion and bromide ion respectively in the mixture of potassium bromide and potassium nitrate and K_{sp} indicates solubility product of silver bromide and l.j.p. the liquid junction potential. Now $a_1 = xcf_+$ and $a_3 = xcf_-$ where f_+ is the activity coefficient of silver ion in silver nitrate and potassium nitrate mixture and f_- that of bromide ion in potassium bromide and potassium nitrate mixture. So equation (1) reduces to

$$E - \frac{2\text{x}2.3026RT}{F} \log(xc) = \frac{2.3026RT}{F} \log f^+ f_- - \frac{2.3026RT}{F} \log K_{sp} + \text{l.j.p} \quad \dots (2)$$

In any series as μ is constant, f_+ and f_- will remain constant throughout. Only x will change. Now L.H.S. (represented by p) of equation (2) when plotted against x gives a straight line (Fig. 1). When

TABLE 1—TEMPERATURE 15°C.

μ=C	x	E	p	q	'L'
0.0500	0.4	0.52919	0.72345		
0.0500	0.3	0.51475	0.72329		
0.0500	0.2	0.49490	0.72358	0.72350	0.73629
0.0500	0.1	0.46050	0.72360		
0.0500	0.05	0.42593	0.72345		
0.0400	0.5	0.53019	0.72445		
0.0400	0.4	0.51884	0.72418		
0.0400	0.3	0.50468	0.72430	0.72430	0.73574
0.0400	0.2	0.48433	0.72409		
0.0400	0.1	0.45022	0.72440		
0.0300	0.5	0.51657	0.72511		
0.0300	0.4	0.50557	0.72519		
0.0300	0.3	0.49147	0.72539	0.72530	0.73520
0.0300	0.2	0.47131	0.72535		
0.0300	0.1	0.43668	0.72514		
0.0200	0.6	0.50703	0.72665		
0.0200	0.5	0.49804	0.72672		
0.0200	0.4	0.48700	0.72676	0.72670	0.73478
0.0200	0.3	0.47268	0.72672		
0.0200	0.2	0.45240	0.72658		
0.0100	0.6	0.47531	0.72935		
0.0100	0.5	0.46599	0.72909		
0.0100	0.4	0.45480	0.72998	0.72840	0.73412
0.0100	0.3	0.44034	0.72880		
0.0100	0.2	0.42037	0.72897		

TABLE 2—TEMPERATURE 25°C.

μ=C	x	E	p	q	'L'
0.0500	0.4	0.51665	0.71767		
0.0500	0.3	0.50191	0.71771		
0.0500	0.2	0.48105	0.71769	0.71770	0.73117
0.0500	0.1	0.44559	0.71785		
0.0500	0.05	0.40968	0.71756		
0.0400	0.5	0.51798	0.71900		
0.0400	0.4	0.50614	0.71862		
0.0400	0.3	0.49136	0.71862	0.71820	0.73025
0.0400	0.2	0.47044	0.71854		
0.0400	0.1	0.43460	0.71832		
0.0300	0.5	0.50341	0.71921		
0.0300	0.4	0.49212	0.71939		
0.0300	0.3	0.47725	0.71931	0.71920	0.72964
0.0300	0.2	0.45620	0.71908		
0.0300	0.1	0.42056	0.71906		
0.0200	0.6	0.49386	0.72113		
0.0200	0.5	0.48455	0.72119		
0.0200	0.4	0.47297	0.72108	0.72090	0.72942
0.0200	0.3	0.45799	0.72088		
0.0200	0.2	0.43735	0.72107		
0.0100	0.6	0.45988	0.72277		
0.0100	0.5	0.45050	0.72276		
0.0100	0.4	0.43891	0.72263	0.72290	0.72891
0.0100	0.3	0.42446	0.72297		
0.0100	0.2	0.40372	0.72306		

x=0, l.j.p.=0. Hence

$$\left[E-\frac{2x2.3026RT}{F}\log(xc)\right]_{x=0}=\frac{2.3026RT}{F}\log f_+ f_- - \frac{2.3026RT}{F}\log K_{sp} \quad ... \quad (3)$$

Using the equation $-\log f_i = AZ_i^2\sqrt{\mu} - \beta_i\mu$ and $\beta_{Ag^+}+\beta_{Br^-}=\beta$ equation (3) Becomes

$$\left[E-\frac{2x2.3026RT}{F}\log(xc)\right]_{x=0}+\frac{2x2.3026RT}{F}A\sqrt{\mu}=\frac{2.3026RT}{F}\beta\mu-\frac{2.3026RT}{F}\log K_{sp} \quad ... \quad (4)$$

Taking all the five series at any temperature, L.H.S. (represented by L) of equation (4) is plotted against

TABLE 3—TEMPERATURE 35°C.

μ=C	x	E	p	q	'L'
0.0500	0.4	0.50463	0.71238		
0.0500	0.3	0.48938	0.71240		
0.0500	0.2	0.46787	0.71243	0.71250	0.72669
0.0500	0.1	0.43115	0.71251		
0.0500	0.05	0.39426	0.71244		
0.0400	0.5	0.50600	0.71375		
0.0400	0.4	0.49403	0.71363		
0.0400	0.3	0.47879	0.71367	0.71348	0.72617
0.0400	0.2	0.45728	0.71369		
0.0400	0.1	0.42030	0.71352		
0.0300	0.5	0.49155	0.71457		
0.0300	0.4	0.47976	0.71464		
0.0300	0.3	0.46421	0.71437	0.71498	0.72589
0.0300	0.2	0.44314	0.71482		
0.0300	0.1	0.40640	0.71490		
0.0200	0.6	0.48164	0.71652		
0.0200	0.5	0.47183	0.71639		
0.0200	0.4	0.46012	0.71653	0.71640	0.72537
0.0200	0.3	0.44481	0.71649		
0.0200	0.2	0.42320	0.71642		
0.0100	0.6	0.44687	0.71855		
0.0100	0.5	0.43722	0.71858		
0.0100	0.4	0.42508	0.71830	0.71840	0.72475
0.0100	0.3	0.40990	0.71840		
0.0100	0.2	0.38850	0.71853		

TABLE 4—TEMPERATURE 45°C.

0.0500	0.4	0.49416	0.70864		
0.0500	0.3	0.47831	0.70855		
0.0500	0.2	0.45623	0.70871	0.70880	0.72375
0.0500	0.1	0.41814	0.70862		
0.0500	0.05	0.38043	0.70891		
0.0400	0.5	0.49484	0.70932		
0.0400	0.4	0.48070	0.70942		
0.0400	0.3	0.46708	0.70956	0.70976	0.72313
0.0400	0.2	0.44475	0.70947		
0.0400	0.1	0.40694	0.70966		
0.0300	0.5	0.48058	0.71082		
0.0300	0.4	0.46859	0.71107		
0.0300	0.3	0.45266	0.71092	0.71125	0.72283
0.0300	0.2	0.43039	0.71087		
0.0300	0.1	0.39283	0.71131		
0.0200	0.6	0.46996	0.71244		
0.0200	0.5	0.45997	0.71245		
0.0200	0.4	0.44776	0.71248	0.71230	0.72175
0.0200	0.3	0.43175	0.71223		
0.0200	0.2	0.40943	0.71215		
0.0100	0 6	0.43428	0.71476		
0.0100	0.5	0.42438	0.71486		
0.0100	0.4	0.41216	0.71488	0.71490	072159
0.0100	0.3	0.39654	0.71502		
0.0100	0.2	0.37406	0.71478		

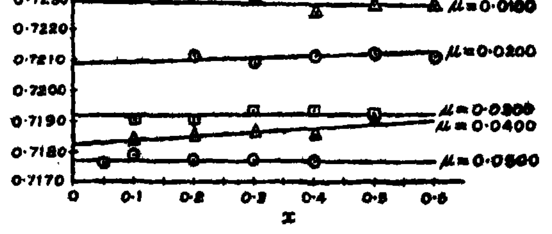


Fig. I Plot of p against x at 25°

μ, a straight line is obtained (Fig. II) and the value of $K_{sp(molarity)}$ is found from the intercept. Using the expression $K_{sp(molality)} = \frac{K_{sp(molarity)}}{p^2}$ where p is the density of water at the temperature concerned, the value of K_{sp} on molality scale was calculated. The results are given in Table-6 along with the values of some other authors.

In the following tables (i) 'E' is the measured value of e.m.f. of the cell in absolute volts, (ii) 'p' stands for $E - \frac{2x2.3026RT}{F} \times \log(xc)$, (iii) 'q' stands

TABLE 5—TEMPERATURE 45°C

μ=c	x	E	p	q	'L'
0.0500	0.4	0.48360	0.70484		
0.0500	0.3	0.46780	0.70530		
0.0500	0.2	0.44478	0.70522	0.70540	0.72115
0.0500	0.1	0.40589	0.70553		
0.0500	0.05	0.36655	0.70539		
0.0400	0.5	0.48405	0.70529		
0.0400	0.4	0.47128	0.70514		
0.0400	0.3	0.45539	0.70551	0.70600	0.72009
0.0400	0.2	0.43232	6.70538		
0.0400	0.1	0.39361	0.70587		
0.0300	0.5	0.46994	0.70744		
0.0300	0.4	0.45732	0.70744		
0.0300	0.3	0.44120	0.70760	0.70743	0.71963
0.0300	0.2	0.41803	0.70735		
0.0300	0.1	0.37891	0.70743		
0.0200	0.6	0.45876	0.70888		
0.0200	0.5	0.44838	0.70882		
0.0200	0.4	0.43561	0.70867	0.70900	0.71896
0.0200	0.3	0.41943	0.70875		
0.0200	0.2	0.39678	0.70904		
0.0100	0.6	0.42180	0.71112		
0.0100	0.5	0.41163	0.71127		
0.0100	0.4	0.39908	0.71134	0.71170	0.71874
0.0100	0.3	0.38292	0.71144		
0.0100	0.2	0.36008	0.71154		

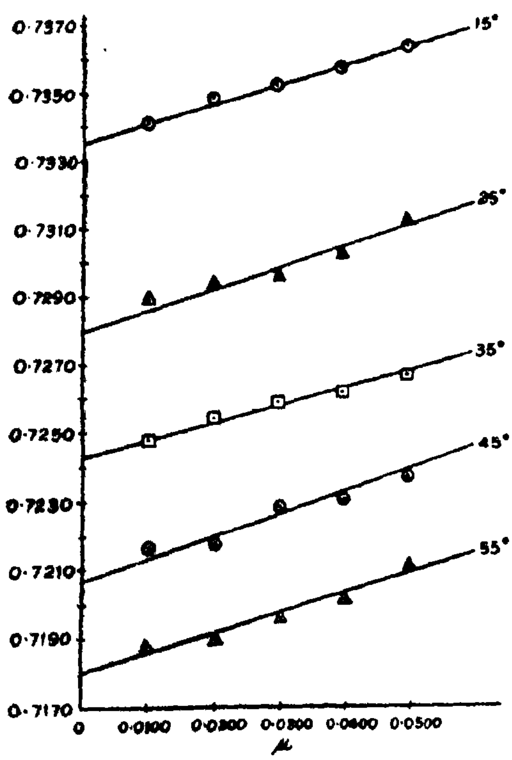


Fig. 11. Plot of ℓ against μ

for extrapolated value of $E - \frac{2x2.3026RT}{F} \times \log(xc)$ when x=0 and (iv) 'L' stands for $q + \frac{2x2.3026RT}{F} - A\sqrt{\mu}$.

The value of E°_{Ag/Ag^+} has been recalculated from K_{sp} value of silver chloride determined by Owen[8] and $E^\circ_{Ag/AgCl, Cl^-}$ determined by Harned and Ehlers[14]. With this value of E°_{Ag/Ag^+} and our value of K_{sp} of silver bromide $E^\circ_{Ag/AgBr, Br^-}$ has been calculated to be 0.0758, 0.0715, 0.0657 and 0.0595 volts at 15°, 25°, 35° and 45° respectively and the values are in fair agreement with those of standard authors[15-21].

A plot of log $K_{sp(molality)}$ against $\frac{1}{T}$ gives a straight line. The value of ΔH is calculated from the slope. The value of ΔG° is calculated from the equation $\Delta G^\circ = -RT \ln K_{sp(molality)}$. Now ΔH is assumed to be equal to ΔH° and ΔS° is calculated. The values given in Table-7 are nearly the same as that of Owen and Brinkley[7] (given in brackets) which are either given in their paper or calculated from their paper.

TABLE 6—SOLUBILITY PRODUCT OF SILVER BROMIDE × 10^{13}

Name of authors		15°C	25°C	35°C	45°C	55°C
Present work	(a) Molarity Scale	1.479	4.948	14.237	38.340	93.867
	(b) Molality Scale	1.481	4.977	14.410	39.099	96.605
Owen and Brinkley[7] (Molality Scale)		1.513	4.982	14.859	40.551	-
Gledhill and Malan[9] (e.m.f. method molality scale)		-	5.015	-	-	-
Gledhill and Malan[6] (Conductometric method-molality scale).		1.48 ±0.28	5.20 ±0.40	16.0 ± 0.5	45.6 ± 0.8	128.2 ± 1.4

TABLE—7

Temp. (°C)	ΔH° in Cals.	ΔG° in Cals.	ΔS° in e.u,
15	20112	17030	10.69
	(20542)	(16899)	(12.64)
25	20112	16898	10.78
	(20150)	(16780)	(11.30)
35	20112	16809	10.72
	(19749)	(16679)	(9.96)
45	20112	16720	10.66
55	20112	16651	10.54

Acknowledgement

We are thankful to the U.G.C. and the Patna University for grants to one of us (A.C.J.) and to the authorities of the Patna University for the library and laboratory facilities.

Referneces

1. GOODWIN, *Z. physik. Chem.*, 1894, 13, 645.
2. THIEL, *Z. anorg. Chem.*, 1900, 24, 57.
3. BODLÄNDER and FITTIG, *Z. physik. Chem.*, 1902. 39, 597.
4. ABEGG and COX, *Z. physik. Chem.*, 1903, 46, 1.
5. A. E. HILL, *J. Amer. Chem. Soc.*, 1908, 30, 68.
6. J. A. GLEDHILL and G. MCP MALAN, *Trans. Faraday Soc.*, 1954, 50, 126.
7. B. B. OWEN and S. R. BRINKLEY, *J. Amer. Chem. Soc.*, 1938, 60, 2233.
8. B. B. OWEN, *J. Amer. Chem. Soc.*, 1938, 60, 2229.
9. J. A. GLEDHILL and G. MCP MALAN, *Trans. Faraday Soc.*, 1953, 49, 166.
10. A. I. VOGEL, "A Text Book of Quantitative Inorganic Analysis including Elementary Instrumental Analysis, Longmans, Third Edn., 1961, page 261, III. 25.
11. H. S. HARNED and S. M. DOUGLAS, *J. Amer. Chem. Soc.*, 1926, 48, 3095.
12. S. NATH, S. ADITYA and B. PRASAD *J. Indian Chem. Soc.*, 1951, 28, 683.
13. G. G. MANOV, R. G. BATES, W. J. HAMER and S. F. ACREE, *J. Amer. Chem. Soc.*, 1943, 65, 1765.
14. H. S. HARNED and R. W. EHLERS, *J. Amer. Chem. Soc.*, 1933, 55, 2179.
15. H. B. HETZER, R. A. ROBINSON and R. G. BATES, *J. Phys. Chem.*, 1962, 66, 1423.
16. H. S. HARNED, A. S. KESTON and J. G. DONELSON, *J. Amer. Chem. Soc.*, 1936, 58, 989.
17. H. K. SINHA and B. PRASAD, *J. Indian Chem. Soc.*, 1970, 47, 901.
18. TOWNS, GREELEY and LIETZKE, *J. Phys. Chem.*, 1960, 64, 1861.
19. B. B. OWEN and L. FOERING, *J. Amer. Chem. Soc.*, 1936, 58, 1575.
20. H. S. HARNED and W. J. HAMER, *J. Amer. Chem. Soc.*, 1933, 55, 4496.
21. H. S. HARNED and J. G. DONELSON, *J. Amer. Chem. Soc.*, 1937, 59, 1280.

J. Indian Chem. Soc.,
Vol. LVII, March 1980, pp. 330-331

Synthesis of N-(2-Methyl-5, 7-Halo-4-Quinazolon-3-yl)-4-Aryl-1-Piperazinylacetamides as Anticonvulsants

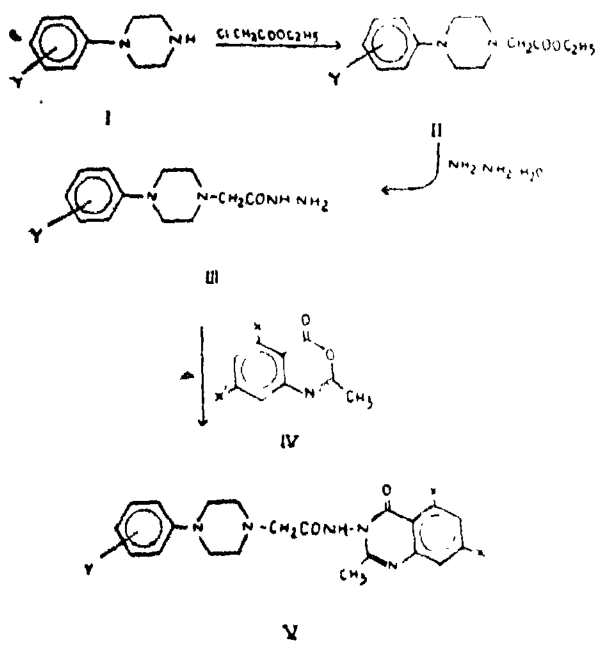
S. S. TEWARI, M. I. HUSAIN* and G. C. SRIVASATVA

Chemistry Department, Lucknow University, Lucknow

Manuscript received 30 April 1979, revised 24 September 1979, accepted 9 January 1980

Twenty new N-(2-methyl-5, 7-halo-4-quinazolon-3-yl)-4-aryl-1-piperazinylacetamides were prepared by the condensation of an appropriate acetanthranil with various 4-aryl-1-piperazinoacetic acid hydrazides. All of these compounds when screened for anticonvulsant activity against pentylenetetrazol-induced seizures in mice at a dose of 80 mg/kg were, however, found to be inactive.

LITERATURE survey has revealed that some derivatives of piperazine[1-5] and quinazolone[6-8] have pronounced anticonvulsant properties. Piperazinoquinazolones[9] have also been reported to possess anticonvulsant activity. In addition a few derivatives of acetamide such as 2,2-dialkylcyanoacetamides[10,11] and in particular 2-ethyl-2-propyl cyanoacetamides have demonstrated significant anticonvulsant activity both against supra maximal electroshock and subcutaneous pentylenetetrazol induced seizures. In view of these observations, the authors have synthesized the title acetamides containing quinazolone and piperazine moieties, the presence of which was expected to enhance anticonvulsant properties. The scheme of their preparation is as follows : (X or X^1 = H, Cl, Br or I and Y = *m*-CH_3 ; *p*-CH_3 ; *m*-Cl and *p*-Cl).



Experimental

Melting points were taken in open capillaries and are uncorrected.

Acetanthranils (IV) : These were prepared by the condensation of an appropriate anthranilic acid[12,13,14] with acetic anhydride according to a reported procedure[15].

N-Aryl-piperazines (I) : These were prepared by the method of Pollard *et al.*[16,17].

4-Aryl-1-piperazinoacetic acid ethylesters(II) and 4-Aryl-1-piperazinoacetic acid hydrazides(III) were prepared according to a known method[18].

III, Y=3-Cl, m.p. 93-94° (60% yield), Found : N, 20.92%. $C_{18}H_{17}N_4OCl$, requires N, 21.30%.

III, Y=4-Cl, m. p. 110-112° (50% yield). Found : N, 20.78%. $C_{18}H_{17}N_4OCl$, requires N, 21.30%.

N-(2-Methyl-5, 7-halo-4-quinazolon-3-yl)-4-aryl-1-piperazinyl acetamides (V) :

A mixture of an appropriate acetanthranil (.01*M*) and 4-aryl-1-piperazinoacetic acid hydrazide (.01*M*) was heated on a free flame for 15-20 mts. On cooling a jelly like mass separated out which was washed with petroleum ether (60-80°). The solid obtained was recrystallised from ethanol (Table 1).

The structures of the above compounds were supported by their IR spectra which showed bands at 3210-3150 cm^{-1} (NH Str.), 1480-1445 cm^{-1} (-CH_2-N<) and 1680 cm^{-1} (C=O of sec. amide).

TABLE 1—N-(2-METHYL-5, 7-HALO-4-QUINAZOLON-3-YL)-4-ARYL-1-PIPERAZINYLACETAMIDES* (V)

Sl. No.	X	X′	Y	m.p. °C	Molecular formula	N % Found	N % Calcd.
1.	Br	H	*p*-CH_3	190	$C_{22}H_{24}N_5O_2Br$	14.51	14.89
2.	Br	Br	*p*-CH_3	195-96	$C_{22}H_{23}N_5O_2Br_2$	12.35	12.75
3.	I	H	*p*-CH_3	108-10	$C_{22}H_{24}N_5O_2I$	13.10	13.53
4.	Br	H	*p*-Cl	63-65	$C_{21}H_{21}N_5O_2ClBr$	13.86	14.27
5.	Br	Br	*p*-Cl	218	$C_{21}H_{20}N_5O_2ClBr_2$	11.81	12.29
6.	I	H	*p*-Cl	132-34	$C_{21}H_{21}N_5O_2ClI$	13.32	13.02
7.	Br	H	*m*-CH_3	148	$C_{22}H_{24}N_5O_2Br$	15.26	14.89
8.	Br	Br	m-CH_3	112-13	$C_{22}H_{23}N_5O_2Br_2$	12.30	12.75
9.	I	H	*m*-CH_3	139-40	$C_{22}H_{24}N_5O_2I$	13.27	13.53
10.	Br	H	*m*-Cl	70	$C_{21}H_{21}N_5O_2ClBr$	13.75	14.27
11.	Br	Br	m-Cl	119-20	$C_{21}H_{20}N_5O_2ClBr_2$	11.85	12.29
12.	Cl	H	*m*-Cl	150	$C_{21}H_{21}N_5O_2Cl_2$	15.37	15.69
13.	I	H	*m*-Cl	148-49	$C_{21}H_{21}N_5O_2ClI$	13.43	13.02
14.	Cl	Cl	*m*-Cl	130-32	$C_{21}H_{20}N_5O_2Cl_3$	14.25	14.56
15.	Cl	Cl	*m*-CH_3	200	$C_{22}H_{23}N_5O_2Cl_2$	14.89	15.21
16.	Cl	H	*p*-CH_3	174	$C_{22}H_{24}N_5O_2Cl$	16.17	16.45
17.	Cl	H	*p*-Cl	150-51	$C_{21}H_{21}N_5O_2Cl_2$	15.56	15.69
18.	Cl	Cl	*p*-Cl	255	$C_{21}H_{20}N_5O_2Cl_3$	14.13	14.56
19.	Cl	H	*m*-CH_3	155	$C_{22}H_{24}N_5O_2Cl$	16.13	16.45
20.	Cl	Cl	*m*-CH_3	125	$C_{22}H_{23}N_5O_2Cl_2$	14.83	15.21

*Yields ranged from 50 to 60%.

Acknowledgement

The authors express their sincere thanks to Dr. R.C. Srimal of C.D.R.I., Lucknow, for anticonvulsant screening of the compounds and to Dr. Kirpa Shankar of K.G.M.C., Lucknow, for helpful discussions. Thanks are also due to Dr. S. P. Tewarson, Principal, Lucknow Christian College, for granting academic leave and the U.G.C. for providing teacher fellowship to one of us (G.C.S.).

References

1. B. LUEKA-SABSTEL and A. ZEI, *Diss. Pharm. Pharmacol.*, 1971, **23**, 135.
2. V. K. AGARWAL, K. C. SAH, S. NAGAR and S. S. PARMAR, *J. Prakt. Chem.*, 1970, **312**, 964.
3. A. K. CHATURVEDI and S. S. PARMAR, *Curr. Sci.*, 1972, **41**, 253.
4. Lakeside Laboratories Inc., *Brit.*, 1963, 936, 764, *Chem. Abs.*, 1964, **61**, 8322f.
5. *Belg. Pat.*. 1963, 623, 058.
6. M. L. GUJRAL, P. N. SAXENA and R. P. KOHLI, *Indian J. Med. Res.*, 1957, **45**. 207
7. C. BIANCHI and A. DAVID, *J. Pharm. Pharmacol.*, 1960 **12**, 501
8. A. K. CHATURVEDI and S. S. PARMAR, *Indian J. Pharm.*, 1972, **34**, 72.
9. SURENDRA S. PARMAR, A. K. CHATURVEDI, A. CHAUDHARY and STANLEY J. BRUMLEV, *J. Pharm. Sci.*, 1974, **63**, 357.
10. HERBERT F. SCHWARTZ II, LEE F. WORRELL and JAMES N. DELGADO, *J. Pharm. Sci.*, 1967, **56**, 80.
11. HERBERT F. SCHWARTZ II, ROBERT G. BROWN, EUGENE ISAACSON and JAMES N. DELGADO., *J. Pharm. Sci.*, 1968, **57**, 1530.
12. MARGARAT M. ENDICOTT, BETTY W. ALDEN and MARY L. SHERRILL, *J. Amer. Chem. Soc.*, 1946, **68**, 1303.
13. ALVIN S. WHEELER and W. M. OATES., *J. Amer. Chem. Soc.*, 1910, **32**, 770.
14. CARL J. KLEMME and JAMES H. HUNTER., *J. Org. Chem.*, 1940, **5**, 230.
15. SURENDRA S. PARMAR and R. C. ARORA., *J. Med. Chem.*, 1967, **10**, 1182.
16. C. B. POLLARD and M. S. AGRUSS., *J. Amer. Chem. Soc.*, 1934, **56**, 2199.
17. C. B. POLLARD and THOMOS H. WICKER Jr., *J. Amer. Chem. Soc.*, 1954, **76**, 1853.
18. A. K. SENGUPTA, K. C. AGARWAL and M. MUSHTAQ., *J. Indian Chem. Soc.*, 1977, **54**, 961.

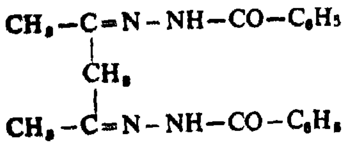
Notes

A Novel Partial Dechlorination of a Pseudo-octahedral *trans* dichloro acetylacetone *bis* (benzoyl-hydrazone) Nickel(II) Complex

R. L. DUTTA and A. K. SARKAR
Department of Chemistry, The University of Burdwan, Burdwan-713 104, W. Bengal, India

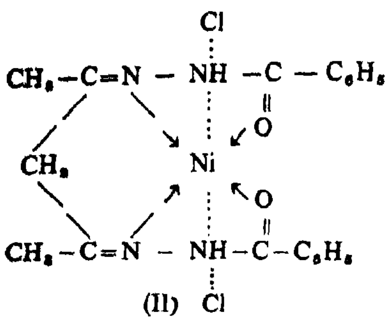
Manuscript received 18 September 1979, accepted 30 December 1979

We have recently described the synthesis[1] of the quadridentate ligand acetylacetone *bis* (benzoyl-hydrazone) (I).

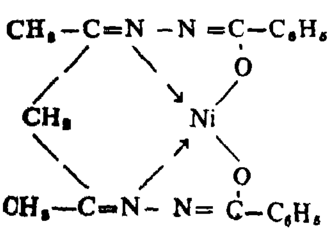


(I)

Under anhydrous condition, the pseudo octahedral sky blue paramagnetic (μ=3.17 BM), non-electrolytic (in nitromethane) complex (II), *trans* dichloro acetylacetone *bis* (benzoyl-hydrazone) nickel(II), can be synthesised while in the presence of a trace of water the ligand undergoes enolisation and an orange-yellow coloured, diamagnetic, square planar non-electrolytic acetylacetone *bis* (benzoyl-hydrazonato) nickel (II) is obtained (III).

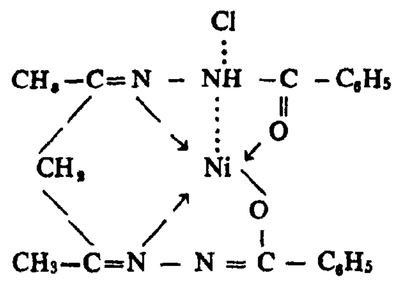


(II)



(III)

It has been now observed that alternate exposure of the skyblue derivative to moist atmosphere followed by keeping over KOH leads to partial dechlorination (in the form of HCl) of the *trans* dichloro acetylacetone *bis* (benzoyl-hydrazone) nickel(II). After a few days, the colour of the complex changes from sky-blue to greenish-yellow and a steady state results. At this stage the complex corresponds to the loss of one co-ordinated chlorine (in the form of HCl) and gives the following analytical results: [Found C=54.0% ; H=4.8% ; N=13.15% ; Cl=8.16% ; Ni=13.61% ; Calc: C=53.11% ; H=4.4% ; N=13.05% ; Cl=8.27% ; Ni=13.68%]. The loss in weight of the dichloro derivative is 7.5% (over KOH at room temperature) (for one HCl ; required : 7.85). The new monochloro derivative is soluble in nitrobenzene and methanol. In nitrobenzene it gives a molar conductance value Λ_M = 1.2 ohm^{-1} cm^2 mol^{-1}, indicating that the chlorine atom is attached in the inner co-ordination sphere. But in methanol, the molar conductance value is 86 ohm^{-1} cm^2 mol^{-1}, giving (1 :1) electrolyte value due to solvolysis[2]. A five-co-ordinate monomeric structure is thus suggested (IV).



(IV)

The mother compound, although six-co-ordinate pseudo-octahedral, has an ill-resolved electronic spectrum with only one band at 25 kK. But the partially dechlorinated complex shows a very rich mull electronic spectrum with bands at 5.8, 7.04, 8.3, 10.5 and 23.5 kK. The bands strongly suggest a five co-ordinated structure (IV)[3]. Infrared spectrum reveals C=N stretch[4] at 1590 cm^{-1} and-NH stretch[5] at 3300-3400 cm^{-1}. Its magnetic moment of 2. 2 B. M. is rather low for a high-spin 5-co-ordinate nickel(II). It may be indicative of an equilibrium between a high-spin and low-spin 5-co-ordinate structures[6].

The most likely explanation is that moisture facilitates partial conversion of the-NH-C=O keto group to the enol form-N=C-OH. The enol (-OH) group then gets hydrogen bonded to one of the two chlorines. KOH assists in extracting and absorbing the HCl, thus converting the compound to a five co-ordinate monochloro acetylacetone (mono benzoyl-hydrazone) (mono benzoyl-hydrazonato) nickel (II). The isolation of this compound exposes a very unusual monoketo mono-enol form (i.e., a monobasic

quadridentate behaviour of the ligand). Thus in the sky-blue (II), greenish-yellow (IV) and orange-yellow compound (III), we have successfully unfolded the neutral, monobasic and dibasic characters of the quadridentate Schiff base (I) respectively.

Experimental

The ligand acetylacetone *bis* (benzoyl-hydrazone) and the complex (II) were prepared according to the procedures of our previous work[1].

Physical measurements

Nickel(II) was estimated as *bis* (dimethylglyoximato) nickel(II). Nitrogen was determined by Duma's method. The chloride was determined as silver chloride, and magnetic moment was obtained from corrected χ_M value, using a Gouy balance with $CuSO_4$, $5H_2O$ as a calibrant. Nujol mull spectra were run by R. S. I. C., Madras. C, H, analyses as also the IR spectra were carried out by C. D. R. I., Lucknow.

References

1. R. L. Dutta and A. K. Sarkar, *Indian J. Chem.*, (Submitted for publication).
2. W. J. Geary, *Coord. Chem. Rev.*, 1971, 7, 81.
3. C. Furlani, *Coord. Chem. Rev.*, 1968, 3, 141.
4. R. L. Dutta and S. P. Banerjee, *J. Indian Chem. Soc.*, 1974, 51, 497.
5. L. El. Sayed and M. F. Iskander, *J. Inorg. Nuclear Chem.*, 1971, 33, 435.
6. J. H. Worrell, J. J. Genova and T. D. DuBois, *J. Inorg. Nuclear Chem.*, 1978, 40, 441.

A Mixed Anion Salt of Beryllium

R. C. SHARMA

Department of Chemistry, Govt. College, Kota (Raj.)

and

(Mrs.) MADHU PHULL*

Department of Chemistry, Indian Institute of Technology, Kanpur-16

Manuscript received 20 November 1978, revised 11 May 1979, accepted 20 December 1979

In past few years many mixed ligand complexes of metals have been studied by different physico-chemical methods. Potentiometric evidences are available for the formation of 1 : 1 : 1 M(II)AB ternary complexes[1-5] where A is usually EDTA and B a secondary ligand like glycine, salicyclic, succinic, tartaric or maleic acid. Survey of the literature however, reveals that ternary complexes without the involvement of EDTA have been studied once[6]. The present paper describes the formation of BeAB system where A is an anion of 3,5-dinitrosalicylic acid (DNS) and B of chromotropic acid (CTA).

DNS[8] and CTA[8] figure prominently in the discussion of hydroxy carboxylic acids and hydroxy acids respectively. Each of DNS and CTA provides two possible interaction sites.

Experimental

Beryllium sulphate, potassium nitrate, sodium hydroxide (all AnalaR grade), Reidel's DNS and disodium salt of CTA (E. Merck) were used. Solutions were prepared in double distilled water. A cambridge bench type pH meter was used for pH measurements.

To know the stoichiometry of the Be-DNS & CTA complex, the proton displacements were evaluated titrating solutions containing Be and the concerned ligands in different ratios employing a standard alkali.

Results and Discussion

The titration curves are shown in figure. Curve

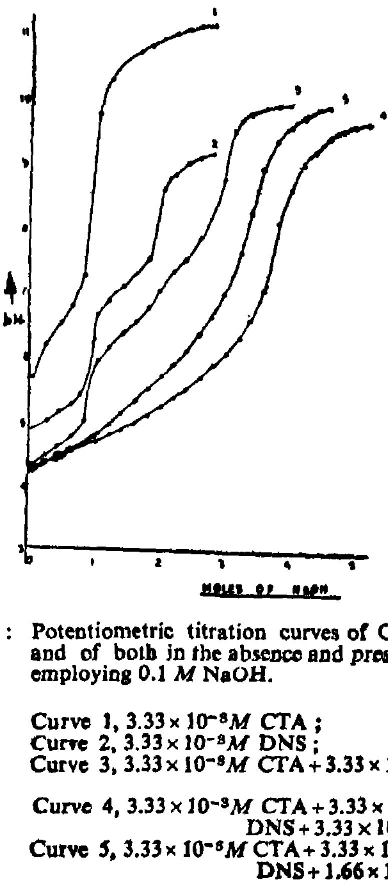


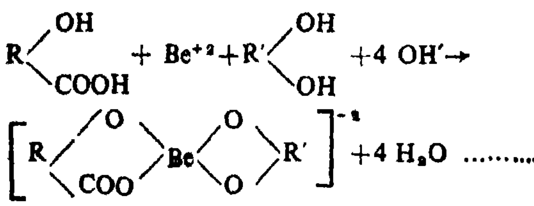
Figure. : Potentiometric titration curves of CTA, DNS and of both in the absence and presence of Be employing 0.1 M NaOH.

Curve 1, $3.33 \times 10^{-3} M$ CTA ;
Curve 2, $3.33 \times 10^{-3} M$ DNS ;
Curve 3, $3.33 \times 10^{-3} M$ CTA + $3.33 \times 10^{-3} M$ DNS ;
Curve 4, $3.33 \times 10^{-3} M$ CTA + $3.33 \times 10^{-3} M$ DNS + $3.33 \times 10^{-3} M$ Be ;
Curve 5, $3.33 \times 10^{-3} M$ CTA + $3.33 \times 10^{-3} M$ DNS + $1.66 \times 10^{-3} M$ Be.

* To whom correspondence should be addressed.

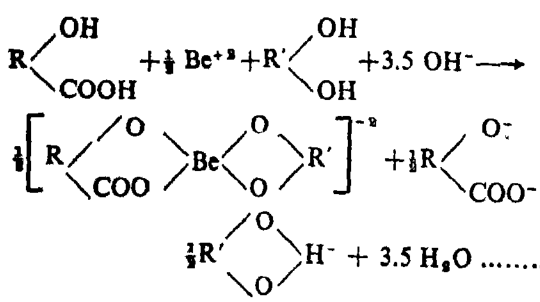
1 shows only one inflection at m=1 which is due to neutralisation of one of the two phenolic-OH groups of CTA(R′(OH)(OH)). The second phenolic -OH is not neutralised due to the formation of intramolecular H-bonding[7]. Curve 2 shows two inflections at m=1 and m=2 which indicate the neutralisation of -COOH and -OH groups of DNS (R(OH)(COOH)).

When 1 : 1 mixture of these ligands is titrated against a standard alkali,) two inflections at m=1 and m=3 (Curve 3) are observed which confirms the above neutralisation patterns. When equimolar concentration of Be is added to a 1 : 1 mixture of these ligands, an inflection at m=4 (Curve 4) is observed which reveals the formation of a 1 : 1 : 1 mixed anion salt as under


(1)

The formation of such a salt is confirmed by the observation that on titration with an alkali a 1 : 1 : ½, DNS, CTA, Be mixture shows an inflection at m=3.5.

The reaction may be represented as follows :


(2)

The formation of this salt appears to justify the 4-fold coordination requirements of the sp^3 hybridised Be.

Acknowledgement

The authors feel grateful to Dr. S.K. Verma, Principal and Shri K.P. Bhargave, Head, Chemistry Department, Govt. College, Kota for providing laboratory facilities. One of the authors (R.C.S.) is also grateful to U.G.C., New Delhi for a financial assistance granted to him.

References

1. D. D. Perrin, I. G. Sayco and V. S. Sharma, *J. Chem. Soc.*, 1967, **11**, 1755.
2. P. R. Shukla and Gopal Narain, *J. Indian Chem. Soc.*, 1967, **44**, 552.
3. G. K. Chaturvedi and J. P. Tandon, *Zeit. Naturforsch*, 1970, **25**, 26.
4. R. C. Sharma, S. S. Dhindsa and D. N. Bhargav, *Monatshefte für chemie*, 1978, **109**, 333.
5. S. S. Dube and S. S. Dhindsa, *Z. Naturforsch.*, 1969, **246b**, 967.
6. R. C. Mehrotra, V. D. Gupta and C. K. Sharma, *J. Indian Chem. Soc.*, 1973, **50**, 207.
7. R. Wake, H. Miyate and Toeik, *Bull. Chem. Soc. Japan.*, 1968, **41**, 1452.

Stepwise Stability Constants and Thermodynamic Functions of Mn(II), Zn(II) and Cd(II) Complexes with 2-Hydroxy-5-chlorobenzophenone-o-tolil (HCBoT)

Y. Z. PATHAK and G. B. JOSHI

Department of Chemistry, Saurashtra University, Bhavnagar

Manuscript received 10 October 1979, accepted 30 December 1979

In continuation of our previous communications[2,3] herein, we describe potentiometric studies on chelates of 2-hydroxy-5-chlorobenzophenone-*o*-tolil (HCBoT) with Mn(II), Zn(II) and Cd(II) in 60% v/v dioxan water media at $\mu = 0.1M$ at 25°, 30° and 35°.

Experimental

The expanded scale *p*H meter of systronic with a wide range (0.01 *p*H glass electrode and a calomel reference electrode was used for *p*H measurements.

The ligand 2-hydroxy-5-chlorobenzophenone-*o*-tolil was synthesised by condensing 2-hydroxy-5-chlorobenzophenone with orthotoluidine. It was crystallised from alcohol, m.p. 157°-159°.

All the chemicals used were of B.D.H. AnalaR grade. The potentiometric titration was carried out in an inert atmosphere using carbonate free sodium hydroxide solution and the constant ionic strength was maintained by adding requisite amount of sodium perchlorate solution. The Calvin-Bjerrum *p*H titration technique[4,5] as used by Irving and Rossotti[1] has been applied to determine the protonation constants of the ligand and the formation constants of complexes. The log K values were computed by various computational methods as summarised in Table 1.

TABLE 1— STABILITY CONSTANTS ON Mn(II), Zn(II) AND Cd(II) CHELATES OF 2-HYDROXY-5-CHLOROBENZOPHENONE o-TOLIL AT μ = 0.1 M IN 60% v/v DIOXANE-WATER MEDIA

Chelates	Temp. °C.		Methods: least square	linear-plot	Bjerrum spreading factor method.
(1)	(2)		(3)	(4)	(5)
$Mn(HCBoT)_2$	25	$\log K_1$	5.66	5.68	4.08
		$\log K_2$	4.20	4.13	4.08
		$\log \beta$	9.86	9.81	9.74
$Mn(HCBoT)_2$	30	$\log K_1$	5.62	5.63	5.64
		$\log K_2$	4.04	4.06	4.06
		$\log \beta$	9.66	9.69	9.70
$Mn(HCBoT)_2$	35	$\log K_1$	5.47	5.52	5.40
		$\log K_2$	3.97	3.90	3.98
		$\log \beta$	9.44	9.42	9.38
$Zn(HCBoT)_2$	25	$\log K_1$	7.87	7.89	7.90
		$\log K_2$	5.36	5.37	5.36
		$\log \beta$	13.23	13.96	13.26
$Zn(HCBoT)_2$	30	$\log K_1$	7.84	7.75	7.70
		$\log K_2$	5.21	5.13	5.20
		$\log \beta$	12.95	12.88	12.90
$Zn(HCBoT)_2$	35	$\log K_1$	7.59	7.60	7.55
		$\log K_2$	5.17	5.20	5.25
		$\log \beta$	12.76	12.80	12.80
$Cd(HCBoT)_2$	25	$\log K_1$	7.74	7.75	7.70
		$\log K_2$	5.30	5.27	5.34
		$\log \beta$	13.04	13.02	13.04
$Cd(HCBoT)_2$	30	$\log K_1$	7.61	7.61	7.64
		$\log K_2$	5.15	5.11	5.10
		$\log \beta$	12.76	12.72	12.74
$Cd(HCBoT)_2$	35	$\log K_1$	7.43	7.49	7.44
		$\log K_2$	5.07	5.03	5.08
		$\log \beta$	12.50	12.52	12.52
HCBoT	25	$\log P_{K_1}^H$	11.01	11.02	11.02
		$\log P_{K_2}^H$	3.73	3.73	3.73
		$\log P_K^H$	19.74	14.75	14.75
HCBoT	30	$\log P_{K_1}^H$	10.97	10.98	10.97
		$\log P_{K_2}^H$	3.68	3.70	3.69
		$\log P_K^H$	14.65	14.68	14.66
HCBoT	35	$\log P_{K_1}^H$	10.93	10.94	10.94
		$\log P_{K_2}^H$	3.64	3.66	3.65
		$\log P_K^H$	14.57	14.60	14.59

TABLE 2—THERMODYNAMIC PARAMETERS OF Mn(II), Zn(II) AND Cd(II) CHELATES OF 2-HYDROXY-5-CHLOROBENZOPHENONE o-TOLIL AT μ = 0.1 M IN 60% v/v DIOXANE-WATER

Chelate	Temp, °C.	*log β average	$-\Delta G$ K cal./mole	$-\Delta H$ K cal./mole	$-\Delta S$ (e.u.)
$Mn(HCBoT)_2$	25	9.86	13.44	16.11	8.96
$Mn(HCBoT)_2$	30	9.66	13.40	16.11	8.94
$Mn(HCBoT)_2$	35	9.44	13.30	16.11	9.12
$Zn(HCBoT)_2$	25	13.23	18.05	19.19	11.21
$Zn(HCBoT)_2$	30	12.95	17.95	19.19	11.35
$Zn(HCBoT)_2$	35	12.76	17.99	19.19	11.04
$Cd(HCBoT)_2$	25	13.04	17.78	21.94	13.96
$Cd(HCBoT)_2$	30	12.76	17.70	21.94	13.99
$Cd(HCBoT)_2$	35	12.50	17.62	21.94	14.03

The values of the changes in free energy (ΔG) enthalpy (ΔH) and entropy (ΔS) accompanying the metal ligand complex forming reaction have been calculated at 25°, 30° and 35° using the relations—

$$\Delta G = -RT \ln K$$

$$\frac{d \log K}{d(1/T)} = \frac{\Delta H}{4.57}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

they are summarised in Table 2.

It is concluded that with the change in temperature there was no appreciable change in the value of stability constants or which almost remain constant.

The order of stability constants of metal complexes as given below are in good agreement with Irving-Williams order

Zn(II) > Cd(II) > Mn(II)

Acknowledgement

The authors are grateful to Prof. K. A. Thaker, Head of the Chemistry Department for providing necessary research facilities. We are also thankful to Saurashtra University for the scholarship to Y.Z.P.

References

1. H. Irving and H. S. Rossotti, *J. Chem. Soc.*, 1953, 3397.
2. Y. Z. Pathak and G. B. Joshi, *J. Inst. of Chemists* (India), 1978, 50, 116.
3. Y. Z. Pathak and J. B. Joshi, *J. Indian Chem. Soc.*, 1979, 56, 210.
4. J. Bjerrum "Metal Ammine Formation in Aqueous Solution" P. Haase and Sons, Copenhagen.
5. Calvin and K. W. Wilson, *J. Amer. Chem. Soc.*, 1945, 67, 2003.
6. H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 1953, 3129.

Mixed Ligand Complexes of Ni(II) with Iminodiacetic Acid (IMDA) as Primary Ligand and Thioglycollic, Thiolactic, Thiomalic Acid and Corresponding Amino Acid as Secondary Ligands

J. D. JOSHI and P. K. BHATTACHARYA*
Department of Chemistry, South Gujarat University, Surat-395 007

Manuscript received 10 October 1979, accepted 30 December 1979

BHATTACHARYA and co-workers[1-4] have investigated the mixed ligand system (MAL) involving bivalent metal ions like Cu^{2+}, Ni^{2+}, Zn^{2+} and Histidine. Iminodiacetic acid, nitrilo tri-acetic acid as primary ligands and polyhydroxy phenols or aminoacids as secondary ligands. Various mixed ligand complexes with IMDA[5] as the primary ligand have been studied. In the present investigation attempt have been made to study the formation constants of the title systems.

IMDA is known to form 1 : 1 complex with Ni(II) at low *p*H and the complex is stable at higher *p*H, where the combination of secondary ligand starts. The reaction can be shown as follows :

$$M^{2+} + AHn \rightleftharpoons MA^{-(n-2)} + nH^{+}$$

$$MA^{-(n-2)} + LH_{M} \rightleftharpoons MAL^{-(n+M-2)} + mH^{+}$$

$$K_{MAL} = \frac{(MAL)}{(MA)(L)}$$

Experimental

All the reagents used were of A. R. quality. Ni(II) perchlorates was prepared from the nickel carbonate and the metal content was determined and checked. All the solutions have been prepared in conductivity water.

Metrohm E 350 A *p*H meter (accuracy +0.05) was used and the titrations were carried out at 30°, using constant temperature bath (accuracy =0.1°).

The nature of the curves can be interpreted as done in earlier publications[6]. In the secondary ligand two equivalent extra acid has been added, in order to account for the extra hydrogen ions liberated due to the combination of primary ligand IMDA. n^{-} and P^{L} can be calculated using same equation as in earlier cases[7]. Precise values of K^{MA}_{MAL} were obtained by using the method of averages[8] ; and the values are presented in Table 1.

Discussion

It is observed that in case of thioacids the values of mixed ligand formation constants $K^{Ni\,IMDA}_{Ni\,IMDAL}$ are lower than K^{Ni}_{NiL}. This may be due to the charge repulsion between primary ligand and secondary ligand. In case of thiomalic acid the differences between K^{Ni}_{NiI} and $K^{Ni\,IMDA}_{Ni\,IMDA \cdot L}$ is more because thiomalate ion has three negative charges and has a bigger size resulting in greater electrostatic repulsion.

In case of amino acids, the order of the formation constants of the reaction MA+L is same as in the binary M+L system. This can be explained in terms of their basicities of the secondary ligands[9-10]. However, the values of $K^{Ni\,A}_{Ni\,AL}$ are significantly lower than the values of $K^{Ni\,A}_{Ni\,L}$. This can be explained to be due to the charge repulsion between the primary

*Faculty of Science, Department of Chemistry, M. S. University, Baroda.

TABLE 1 – MIXED LIGAND COMPLEX FORMATION CONSTANTS OF SOME HETEROCHELATES OF Ni(II) AT 30°

L	$\log K^{Ni.IMDA}_{Ni.IMDA.L}$	L	$\log K^{Ni.IMDA}_{Ni.IMDA.L}$
Thioglycollic acid.	5.34±0.02	Glycine	4.85±0.03*
Thiolactic acid.	5.94±0.02	α-Alanine	4.59±0.02*
Thiomalic acid.	5.91±0.01	Aspartic acid.	5.18±0.04

*Values taken from literature—Reference No. 3.

ligand and secondary ligand. The values of $\log K^{Ni}_{NiL}$-$\log K^{Ni.IMDA}_{Ni.IMDA.L}$ where L=aspartic acid is higher because aspartic acid has two negative charges and hence the repulsion between the primary charged ligand ion and secondary ligand ion is still more.

It is observed that in the (Ni. IMDA. thio-acid) systems, the behaviour of thioacids is similar to that of the σ-bonding amino acids. The $\log K^{Ni}_{NiL}$-$\log K^{Ni.IMDA}_{Ni.IMDA.L}$ values are nearly same for the pairs of glycine-Thioglycollic acid, α-alanine-thiolactic and aspartic acid-thiomalic acid. This indicates that in both the cases the factor responsible for the lowering of the values of $K^{Ni\ IMDA}_{Ni\ IMDA\ L}$ is electrostatic repulsion. The situation should have been different if there would have been significant Ni→S π interaction in the thio acid complexes. Therefore, the role of Ni→S π-interaction, if present, is not very significant. The strengthining of Ni→S bond in the mercapto acid complexes is due to σ-interactions as explained by Jorgenson and Klopman[11-12].

References

1. I. P. MAVANI, C. R. JEJURKAR and P. K. BHATTACHARYA, *Indian J. Chem.*, 1972, **10**, 742.
2. M. V. CHIDAMBARAM and P. K. BHATTACHARYA, *Acta Chim. Hung.*, 1975, **75**, 123.
3. J. D. JOSHI, *Indian J. Chem.*, 1977, **15A**, 57.
4. J. D. JOSHI and P. K. BHATTACHARYA, *J. Indian Chem. Soc.*, 1973, **50**, 344.
5. B. E. LEACH and R. J. ANGELICI, *Inorg. Chem.*, 1969, **8**, 907.
6. B. R. PANCHAL and P. K. BHATTACHARYA, *J. Inorg. Nuclear Chem.*, 1972, **49**, 469.
7. I. P. MAVANI, C. R. JEJURKAR and P. K. BHATTACHARYA, *J. Indian Chem. Soc.*, 1972, **49**, 469.
8. S. N. DUBEY and R. C. MEHROTRA, *J. Indian Chem. Soc.*, 1966, **43**, 73.
9. M. V. CHIDAMBARAM and P. K. BHATTACHARYA, *J. Indian Chem. Soc.*, 1970, **47**, 881.
10. M. V. CHIDAMBARAM and P. K. BHATTACHARYA, *Indian J. Chem.*, 1970, **8**, 941.
11. C. K. JORGENSON, Structure & Bonding, 1967, **3**, 106.
12. G. KLOPMAN, *J. Amer. Chem. Soc.*, 1968, **90**, 223.

Polarographic Reduction of Zn(II) and Mn(II) in the Presence of Aqueous Mixtures of Propylene Carbonate

H. C. GOEL*, M. C. DUBEY and MUKHTAR SINGH

Chemical Laboratories, Agra College, Agra

Manuscript received 26 September 1978, revised 21 August 1979, accepted 9 February 1980

PROPYLENE carbonate which has a fairly high dielectric constant[1] (ε 25° = 64.92) is a new solvent in so far as the polarography of inorganic depolarizers in organic solvents is concerned[2]. A survey of literature reveals that polarographic behaviour of inorganic depolarizers in aqueous mixtures of this solvent still remains untouched. With this aim in view a polarographic study of the behaviour of Zn(II) and Mn(II) in aqueous mixtures of propylene carbonate has been undertaken.

Experimental

$ZnCl_2$, $MnCl_2$, KCl were of B.D.H., A.R. grade. Porpylene carbonate was a 'Riedel' product. All the solutions were prepared in conductivity water. The concentration of each depolarizer in the solutions was maintained at $1.0\times10^{-n}M$ and that of the supporting electrolyte (KCl) at 0.1 *M*. A manual polarograph (Toshniwal CLO2) in conjunction with polyflex galvanometer (Toshniwal PL50) was used. Triton X-100 (0.002%) was used to suppress the maximum of Mn(II). Since no maximum appeared in the case of Zn(II) in the present study, addition of suppressor was avoided. The temperature was kept at 25 ± 0.1°. The d.m.e. had the following characteristics (in 0.1 *M* KCl, open circuit): m = 2.34 mg/sec, t = 3.8 sec, $m^{2/3} t^{1/6} = 2.2010$ $mg^{2/3}$ $sec^{-1/2}$ h_{corr} = 58.50 cm.

The number of electrons (n) involved in the electro-reduction of Zn(II) and Mn(II) being well established (n=2), Ilkovic equation was used to calculate the value of 'D' at different percentages of propylene carbonate in aqueous mixtures. The kinetic parameters of the electrode reaction of Zn(II) and Mn(II), wherever found irreversible, were calculated by Koutecky's treatment[3-4].

*Department of Chemistry, Hindu College, Moradabad.

Results and Discussion

Figs. 1 and 2 depict the morphology of C-V curves of Zn(II) and Mn(II) in the presence of increasing percentages of propylene carbonate. The waves are well defined. However, the waves

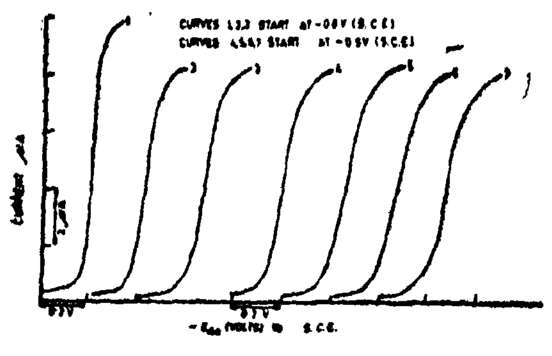


Fig. 1. Polarograms of Zn(II) in the presence of different percentages (v/v) of propylene carbonate :

1. 0%, 2. 2%, 3. 4%, 4. 6%, 5. 10%, 6. 15%, 7. 20%.

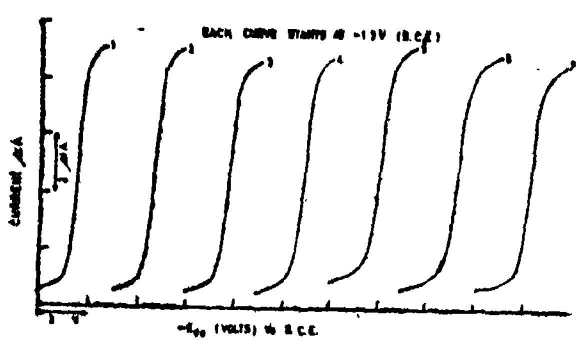


Fig. 2. Polarograms of Mn(II) in the presence of different percentages (v/v) of propylene carbonate :

1. 0%, 2. 2%, 3. 4%, 4. 6%, 5. 10%, 6. 15%, 7. 20%.

could not be obtained at percentages greater than 20 as propylene carbonate was not miscible with water beyond this stage.

The plots of i_d vs. $h^{1/2}_{corr}$ and those of i_d vs. C are linear and pass through the origin thereby showing the diffusion-controlled nature of the electrode processes at different percentages of propylene carbonate.

It has been observed that i_d tends to decrease with increasing percentages of the organic solvent but the fact remains that this decrease is not much remarkable. As it is well known, the change occurring in i_d of a depolarizer is attributed to changes in diffusion coefficient, viscosity and ionic interaction the possibility of which increases with change in dielectric constant. Interionic attraction may appreciably alter the ionic diffusion coefficient as compared to that in water. Since the dielectric constant of propylene carbonate (ϵ 25°=64.92) is in close proximity to that of water (ϵ25°=78.54), the interionic attraction may not take place to an appreciable extent due to fairly high dielectric constant of propylene carbonate and consequently the diffusion coefficients of Zn(II) and Mn(II) are not altered appreciably.

$E_{1/2}$ values of both Zn(II) and Mn(II) get shifted to more negative potentials with increasing percentages of propylene carbonate. The total shift in $E_{1/2}$ of Mn(II) is 55 mV from the value in absence of organic solvent while in the case of Zn(II) it is 176 mV under the same experimental conditions. This significant negative shift in $E_{1/2}$ of Zn(II) vis-a-vis large increase in slope values (from 37 mV in the absence of propylene carbonate to 100 mV in the presence of 20% propylene carbonate) and '$E_{3/4}$-$E_{1/4}$' values (from 37 mV in the absence of propylene carbonate to 95 mV in the presence of propylene carbonate) imply inhibition[5] of the electrode reaction of Zn(II) as compared to that of Mn(II).

The slope value and '$E_{3/4}$-$E_{1/4}$' values for Zn(II) and Mn(II) are of the order of 40+2 mV which indicate that in aqueous medium the electrode reactions of Zn(II) and Mn(II) are quasi-reversible[6-11]. However, with the addition of increasing amounts of propylene carbonate the slope values and '$E_{3/4}$-$E_{1/4}$' values record a sharp increase in respect of the electrode reaction of Zn(II) as compared to that of Mn(II). On applying the criterion of total irreversibility[12] it has been found that 'α' is less than 0.5 at different percentages of propylene carbonate in the case of Zn(II) thereby suggesting that the electrode reaction of Zn(II) becomes totally irreversible in the presence of aqueous mixtures of this solvent. In the case of Mn(II), on the other hand, 'α' is not less than 0.5 signifying that the electrode reaction of Mn(II) does not change from quasireversibility to total irreversibility. Yet an increase in slope values and '$E_{3/4}$-$E_{1/4}$' values does indicate that the electrode reaction of Mn(II) tends to irreversibility with increasing amounts of propylene carbonate.

The values of α n_a in the presence of 2, 4, 6, 10, 15 and 20 precent (v/v) propylene carbonate are respectively : 0.98, 0.81, 0.77, 0.59, 0.51 and 0.40 ; while those of $k^o_{f,h}$ (cm/sec) are : 1.60×10^{-8}, 3.45×10^{-9}, 2.13×10^{-9}, 4.38×10^{-10}, 3.16×10^{-10} and 7.35×10^{-11}. A perusal of αn_a values reveals that the product 'αn_a' records a decrease with increasing percentages of propylene carbonate. The polarographic reduction of Zn(II) is a well-established two-electron process and therefore, the number of electrons involved in the rate determining step can either be 1 or 2. Since the decrease in 'αn_a' values is indiscrete and at no stage the two consecutive values vary by a factor of 2, the possibility of decrease in

the value of the product 'αn_a' due to a change in 'n_a' may be ruled out. Thus, it can be safely concluded that it is 'α' which is decreasing. 'α', the transfer coefficient signifies[13] the fraction of the applied voltage which favours the cathodic reaction, $Zn^{2+} + 2e \rightarrow Zn$. A decrease in the value of 'α' thus implies that the transfer of electron/electrons is made increasingly difficult. In other words the electrode reaction of Zn(II) is rendered increasingly irreversible with increasing percentages of propylene carbonate. The shift in $E_{1/2}$ to more negative potentials and increase in slope values of log plots are also in agreement with the above conclusion.

A decrease in the value of $k^{o}_{f,h}$ with increasing percentages of propylene carbonate lends support to the conclusion arrived at on the basis of 'αn_a' values.

Acknowledgment

Thanks are due to the Principal, Agra College, Agra for the facilities.

References

1. R. PAYNE and I. E. THEODORON, *J. Phys. Chem.*, 1972, 76, 2892.
2. R. TAKAHASHI, *Talanta*, 1965, 12, 1211.
3. J. KOUTECKY, *Chem. Listy*, 1953, 47, 323 : *Colln. Czech. Chem. Commun.*, 1953, 18, 597.
4. J. KOUTECKY and J. CRZEK, *Coll. Czech. Chem. Commun.*, 1956, 21, 836.
5. J. HEYROVSKY and J. KUTA, "Principles of Polarography", Academic Press, New York, 1966, p, 299.
6. J. N. GAUR, D. S. JAIN and A. KUMAR, *Indian J. Chem.*, 1975, 13, 165.
7. P. S. VERMA, D. S. JAIN and J. N. GAUR, *Indian J. Chem.*, 1975, 13, 586.
8. P. DELAHAY, *J. Amer. Chem. Soc.*, 1953, 75, 1430.
9. H. MATSUDA and Y. AYABE, *Z. Elektrochem.*, 1959, 63, 1164.
10. J. KORYTA, *Electrochim Acta*, 1962, 6, 67.
11. P. J. GELLINGS *Z. Elektrochem., Ber., Busenges, Phys. Chem.*, 1962, 66, 477, 481, 799 ; 1963, 67, 167.
12. R. GOTO and I. TACHI, Proc. Intern. Polarogr. Congr., 1951, Vol. I. p. 69.
13. P. DELAHAY, 'New Instrumental Methods in Electro-Chemistry', Interscience Publ., New York, 1954, p. 33.

Standard Heat of Formation of Thorium Tetraacetate†

LAMBODAR THAKUR,* A.K. THAKUR, R. PRASAD and M. F. AHMAD

Post-Graduate Department of Chemistry, Bhagalpur University, Bhagalpur-812 007 (INDIA)

Manuscript received 10 October 1979, accepted 30 December 1979

WE report in this work the heats of solution of crystalline thorium tetraacetate, $ThAc_4$ (c), and pure acetic acid, HAc($Ac=CH_3COO$) in 1*M*-and 6*M*-HCl solutions respectively at 298K. The standard heat of formation of $ThAc_4$(c) can be evaluated by considering the following thermochemical reactions :

$$ThAc_4(c)+4HCl\ (\text{in}\ x\ M\text{-HCl})=Th^{4+}(soln)+4Cl^-(soln)+4HAc(soln)\ ;\ \Delta H_1 \quad (1)$$

$$HAc(l)+x\ M\text{-HCl} = HAc(soln)\ ;\ \Delta H_2 \quad (2)$$

$$ThCl_4(c)+x\ M\text{-HCl} = Th^{4+}(soln)+4Cl^-(soln)\ ;\ \Delta H_3 \quad (3)$$

As the ionization constant of acetic acid is of the order of 10^{-5}, it would dissolve in HCl solution without ionization as shown in Eq.(2).

From the above equations, we find

$$\Delta H_f{}^\circ ThAc_4(c)=-(\Delta H_1-4\Delta H_2)+\Delta H_f{}^\circ Th^{4+}(\text{in}\ x\ M\text{-HCl})+4\Delta H_f{}^\circ HAc(l) \quad (4)$$

and

$$\Delta H_f{}^\circ ThAC_4(c)=-(\Delta H_1-4\Delta H_2-\Delta H_3)+\Delta H_f{}^\circ ThCl_4(c)+\Delta H^\circ{}_f HAc(l)-4\Delta H_f{}^\circ HCl(\text{in}\ x\ M\text{-HCl}) \quad (5)$$

Experimental

Thorium tetraacetate was prepared by refluxing a mixture of BDH 'AnalaR' crystalline thorium nitrate pentahydrate, $Th(NO_3)_4, 5H_2O$(c), with a 2 : 1 mixture of glacial acetic acid and acetic anhydride for several hours[1]. A white crystalline solid separated which was washed several times with glacial acetic acid in a fritted-glass filter stick. The final product was vacuum dried at 60° for several hours until there was no loss in weight of the sample. It was analysed for thorium (Found : Th, 49.3 ; Calc. for $ThAc_4$(c) : Th,49.6%). 'AnalaR' glacial acetic acid was triply distilled under reduced pressure before use.

TABLE 1—HEATS OF SOLUTION OF THORIUM TETRAACETATE AND ACETIC ACID IN 175 ML AQUEOUS HYDROCHLORIC ACID AT 298K IN KJ MOL^{-1}.

Solvents	Compounds	Weight (gms.)	Concn. (mole/l)	ΔH (kJ mol^{-1})	Mean
1*M*-HCl	$ThAc_4$(c)	0.25076	0.00306	—45.0	
		0.35125	0.00429	—46.5	—46.1±0.2
		0.38148	0.00466	—46.0	
6*M*-HCl	$ThAc_4$(c)	0.14216	0.00173	—36.0	
		0.17867	0.00218	—35.8	—35.7±0.5
		0.19078	0.00232	—35.2	
1*M*-HCl	HAc(l)	1.5500	0.148	—0.80	
		1.6671	0.159	—0.80	- 0.80
		1.8631	0.177	—0.80	
6*M*-HCl	HAc(l)	1.6903	0.161	- 0.5	
		1.9236	0.183	- 0.5	- 0.5
		2.3759	0.226	- 0.6	

A closed-system calorimeter described earlier was

† Paper presented at the Annual convention of Chemists. Kurukshetra, Sept. 23-26, 1979.

used[4]. The temperature sensor was a 10kΩ-thermistor and the calorimeter was calibrated electrically with the help of a manganin heater.

Results and Discussion

Table 1 presents the heats of solution values. The average values for ΔH_1 in $1M$- and $6M$-HCl respectively are -46.1±0.2 and -35·7 ±0·5 kJ mol^{-1}. The average values for ΔH_2 in the corresponding acid solutions are -0.5 and -0.8 kJ mol^{-1} respectively. The heat of solution of $ThCl_4$(c) in $1M$- and $6M$-HCl reported previously[3] are -241.8±0.7 and -188.3±0.4 kJ mol^{-1} respectively and ΔH_f °$ThCl_4$(c) also known from this latter source is -1184 4±1.0 kJ mol^{-1}. The differential heat of formation of hydrochloric acid in $1M$-HCl and $6M$-HCl solutions are -164.4±0.1 and -153.4±0.2 kJ mol^{-1} respectively[3]. The standard heat of formation of Th^{4+} in $1M$- and $6M$-HCl respectively are -768.6.±1.7 and -759.0±0.8 kJ mol^{-1} respectively[3]. From Cox and Pilcher[4], ΔH_f °HAc(l) = -484.5±2.0 kJ mol^{-1}. Substituting the above values in Eqs.(4) and (5), we get ΔH_f °$ThAc_4$(c) = -2662±5 and -2665±5 kJ mol^{-1} respectively. The mean of the two values gives ΔH_f °$ThAc_4$(c) = -2663+5 kJ mol^{-1}.

References

1. R. N. KAPOOR, K. C. PANDE and R. C. MEHROTRA, *J. Indian Chem. Soc.*, 1958, 35, 157.
2. L. THAKUR, M. F. AHMAD and R. PRASAD, *Indian J. Chem.*, 1978, 16A, 661.
3. J. FUGER and D. BROWN, *J. Chem. Soc. Dalton*, 1973, 428.
4. J. D. COX and G. PILCHER, *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, New York, 1970, p. 223.

Mössbauer Spectra of Tl(III) hexacyanoferrate(III)

D. KISHORE, G. P. GUPTA, K. C. LAL
Department of Physics, Lucknow University, Lucknow
and
T.N. SRIVASTAVA
Department of Chemistry,
Lucknow University Lucknow.
(U.P.) India

Manuscript received 23 May 1979, accepted 19 November 1979

THE C≡N ligand very often gives rise to linkage isomerism yielding C bonded and N bonded metal complexes. Allen and Bonnette[1] observed that in samples of prussian blue containing various interstitial cations the flipping of CN ligand or exchange of cations occurs around 250°. The phenomenon of cyanide linkage isomerism has also been investigated in iron(III) hexacyanochromate (III)[2] in which chromium(III) is associated with the C end of the ligands but even at room temperature the nature of bonding is found to change spontaneously yielding Fe(II) bonded through C holes and Cr(III) through N-holes. The identical structure of prussian blue and turnbull's blue[3] has been explained on the basis of valence oscillation resonancie between two structures in which the charge transfer from Fe^{3+} (high spin) to Fe^{2+} (low spin) or flipping of C≡N ligand occurs at the instant of combination.

In order to explore the phenomenon of linkage isomerism in double metal cyanide, we choose to examine the Mössbauer Spectra of a complex of iron(III) with Tl(III) where there is least possibility of electron transfer from one metal to the other. The results are reported in this short communication.

Experimental

Thallium(III) hexacyanoferrate (III) was prepared by double decomposition between Thallium(III) perchlorate and potassium ferricyanide. The hot concentrated solutions of the two reactants were mixed and heated to boiling. The dark blue precipitate was separated, washed several times with water, ethanol and finally with ether. The sample was dried in vacuum and its composition Tl $[Fe(CN)_6]$ was established through elemental analysis. The I. R. spectrum of the sample was recorded in K Br between 4000 to 650 cm^{-1} using Perkin-Elmer Spectrometer model-337 and a strong peak at 2100 cm^{-1} assigned to νC≡N is observed.

The Mössbauer spectra were recorded at room and liquid air temperatures on a spectrometer employing proportional counter, a single channel analyser and mechanical drive using constant velocity cams. The source used was co^{57} in Cu matrix.

Results and Discussion

The observed experimental results are summarised below :-

Chemical shift $\delta = +0.68$ mm/sec. (NP)

Quadrupole splitting $\Delta = 1.20$ mm/sec.

The Δ is almost temperature independent and the Mössbauer fraction is low at room temperature, as shown in the figure 1.

The observed chemical shift in the complex is around that reported for the highly ionic $FeCl_3$ and FeF_3. The value therefore suggests that Fe(III) in our complex is at least partly high spin which is improbable if the Fe is completely in the C-holes.

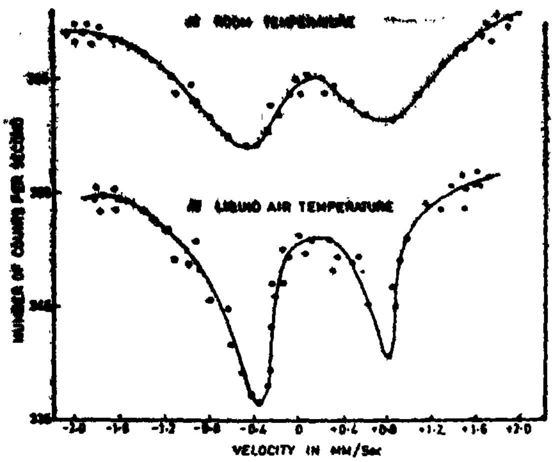


Fig. 1

A comparison of the observed Δ value with those of other heavy metal hexacynoferrates(III) indicates an abnormally high value. Moreover Δ is temperature independent which is the characteristic of a high spin state. The abnormally high value of Δ suggests that all Fe(III) in the complex under investigation may not be in the low spin state and may be partly in the form of polarized Fe^{3+}. This is possible if we assume a resonance of the following type between two structure $Tl[Fe(CN)_6] \leftrightharpoons Fe[Tl(CN)_6]$ in which Tl(III) has exchanged with Fe(III) in the coordination sphere. Such an exchange is likely to cause ligand isomerism, since Fe(III) has stronger tendency to bond through C while Thallium(III) prefers nitrogen bonding. Such a resonance having isocyanide structure will result in high distortion of the octahedral symmetry which will consequently increase the quadrupole splitting. It can therefore be safely concluded that there is a possibility of the co-existence of the high spin Fe^{3+} and the low spin Fe(III) in the complex, a conclusion reached earlier on the basis of Magnetic susceptibility measurements in the case of iron (II)-*bis*-(i, 10-phenanthroline)[4]. Moreover, the actual spectrum is an asymmetric doublets due to the superimposition of quadrupole doublets for the low spin Fe(III) and high spin Fe^{3+} and as such high value of Δ is observed similar to the case of prussian blue reported by Maer and Beasley[5].

Acknowledgement

The authors are grateful to Dr. B. G. Gokhale, Lucknow University for the interest and encouragement throughout the work. One of the authors D. Kishore is also thankful to S.C.S,T., U.P. for financial assistance.

References

1. J. F. Allen and A. K. Bonnette, *J. Inorg. Nuclear Chem.*, 1974, **36**, 1011.
2. D. B. Brown and D. F. Shriver, *Inorg. Chem.*, 1969, **8**, 37.
3. A. Ito, M. Suenaga and K. Ono, *J. Chem. Phys.*, 1968, **48**, 3597.
4. E. Konig and K. Madeja, *Chem. Commun.*, 1966, 61.
5. K. Maer Jr. and M. L. Beasley, *J. Amer. Chem. Soc.*, 1960, **90**, 3201.

Cadmium(II) and Mercury(II) Complexes with N-N'-Diphenylthiocarbazide

BIPIN B. MAHAPATRA, A. PANDA, S. S. DASH and S. K. PUJARI

Department of Chemistry, Panchayat College, Bargarh, Sambalpur, Orissa.

Manuscript received 30 August 1979, accepted 30 December 1979

COMPLEXES of Zinc, Cadmium and Mercury(II) with sulphur ligands are of considerable interest as potential fungicides. Earlier complexes of substituted thiourea, dithiourea and mixed ligand complexes[1,2] of thiourea and nitrogen bases have been reported. While studying complexes of d^{10} metal ions with sulphur ligands, ligands containing both sulphur and nitrogen donor sites aroused our interest. As a part of this programme, in recent communication, we have reported[3-4] complexes of substituted thiocarbamides of divalent metal ions. In the present communication several Hg(II) and Cd(II) complexes with N-N'-diphenyl thiocarbazide have been described.

Experimental

All the chemicals used are of AnalaR grade.

Synthesis of the ligand: Phenyl hydrazine (5.16 ml) was added slowly into a beaker containing carbondisulphide (2 ml) kept in the freezing mixture when an exothermic reaction took place with the formation of white solid N-N'-diphenyl thiocarbazide. It was then recrystallized from rectified spirit when white crystalline compound separated out which was then filtered, washed with ethanol and dried in vacuum.

Preparation of complexes: Ethanolic solution of metal halides were reacted separately with ethanolic solution of the ligand in 1 : 2 ratio and refluxed for 1 hr. On cooling white crystalline solid complexes separated out which were then filtered, washed with ethanol and dried in vacuum.

Metal, sulfur and nitrogen in the complexes were estimated by standard methods. Conductance was measured in $M/_{1000}$ acetone solution of the complexes using Toshniwal conductivity bridge. IR spectra were recorded in kBr phase using Beckman IR-20 and Perkin-Elmer-621 spectrophotometer. Relevant analytical and spectral data are recorded in Table 1.

Results and Discussion

All the complexes reported in the present investigation have the general composition $[MLX_2]$, where M = Cd(II), Hg(II), X is Cl^-, Br^-, I^-, NO_3^-, SCN^- and L is N-N'-diphenyl thiocarbazide except the perchlorate complex which has the formula $[CdL_2]X_2$. These are white crystalline solids, have relatively low melting points and are soluble in acetone in which medium the Λ_M values are in the range of 8-12 mhos cm^2 indicating non-electrolytic nature of these complexes. Perchlorate complex has

TABLE 1—M.P. ANALYSIS, CONDUCTANCE AND IR SPECTRAL DATA

Compound	M.P. °C	% Metal Found	% Metal Reqd.	% Sulphur Found	% Sulphur Reqd.	% N Found	% N Reqd.	ΔM mhos cm²	ν(C=S)	ν(NH)	ν(M-S)	ν(M-N)
L	150	-	-	12.49	12.28	21.70	21.57	-	1210	3150 3350	-	-
[$HgLCl_2$]	202	37.88	37.43	6.04	5.86	10.57	10.32	8.00	1190	3100 3280	260	350
[$HgLBr_2$]	225	32.43	32.07	5.17	5.04	9.05	8.69	11.5	1185	3120 3250	285	365
[$HgLI_2$]	167	28.15	28.10	4.49	4.31	7.86	7.54	12.00	1190	3130 3255	270	360
[$HgL(NO_3)_2$]	207	34.43	34.19	5.49	5.27	14.40	14.17	9.5	1180	3100 3260	265	380
$HgL(SCN)_2$]	220	34.91	34.58	16.74	16.58	14.74	14.43	10.6	1190	3110 3275	260	375
[$CdLCl_2$]	244	25.47	25.10	7.25	7.07	12.78	12.56	8.9	1185	3100 3265	290	380
[$CdLBr_2$]	252	21.11	20.89	6.03	6.01	15.61	15.29	10.5	1180	3105 3275	260	375
[$CdLI_2$]	240	18.00	17.53	5.08	4.85	8.89	8.57	11.0	1185	3100 3280	270	370
[CdL_4] $(ClO_4)_2$	250(d)	13.58	13.27	7.44	7.58	13.52	13.28	21.2	1185	3100 3270	280	360

L = N-N¹-diphenyl thiocarbazide.

the conductance value 212 mhos cm² suggesting 1 : 2 electrolytic nature of this compound.

IR spectra of the ligand and the complexes are quite informative. The ligand has two absorption bands in the 3150 and 3350 cm^{-1} region assignable to ν (N-H), in the 1500-1600 region assignable to δ (NH), a band at 1470 cm^{-1} due to ν (C-N) and at 1210 due to ν (C=S). In addition, it has several bands in the 700-1400 region probably due to coupled C-N and C-S vibrations[5]. In the complexes ν (N-H) is observed ~3100-3280 cm^{-1} (several bands). ν (C-N) ~1460 and ν (C=S) ~1190 cm^{-1} region. Splitting of ν (N-H) band and decrease of ν (C-N) and ν(C=S) to lower frequency regions provide evidence of bonding through thiocarbonyl sulfur and nitrogen of one of the -NH groups. This has been further substantiated by observation[6] of ν(M-S) and ν(M-N) ~260-290 and ~ 350-380 cm^{-1} region.

In the thiocyanato complex ν'(C≡N) is observed at 2130 cm^{-1}. An increase of more than 50 cm^{-1} compared to KNCS indicates the thiocyanato group to be terminally S-banded on the basis of earlier observation[7]. In the nitrato complex the ν_4 (NO_2 asymetric stretch) and ν_1 (NO_2 symmetric stretch) bands are observed at 1400 and 1280 cm^{-1} and the difference (Δν) is 120 cm^{-1} indicating the presence of monodentate nitrato group, in conformity with earlier studies[8-9]. In case of the perchlorate complex, a broad band appears at 1100 cm^{-1}. It is known that co-ordinated perchlorate group shows three distinct bands at 1155, 1080 and 1005 cm^{-1} and ionic perchlorate gives rise to a broad absorption band in the 1060-1150 cm^{-1} region. Hence the perchlorate complex contains ionic perchlorate group in conformity with earlier observations[10] and molar conductance data.

Hence all the Cd(II) and Hg(II) complexes reported in the present investigation presumably have a tetrahedral environment around the metal ions.

References

1. B. B. MAHAPATRA, B. K. MAHAPATRA and S. GURU, *Indian J. Chem.*, 1977, **15A**, 746.
2. B. B. MAHAPATRA, B. PAUL and S. GURU, *J. Indian Chem. Soc.*, 1977, **54**, 337.
3. B. B. MAHAPATRA, B. K. MAHAPATRA and S. GURU, *J. Indian Chem. Soc.*, 1978, **55**, 229.
4. B. B. MAHAPATRA, B. K. MAHAPATRA and S. GURU, *Indian J. Chem.*, 1978, **16A**, 445.
5. R. N. SILVERSTEIN and G. C. BASSLER, "Spectrometric Identification of Organic Compounds" John Wiley, New York, 1367.
6. J. R. Ferraro, "Low Frequency vibrations of inorganic and cordination compounds" Plenum Press, New York, 1971.
7. A. TRAMER, *J. Chem. Phys.*, 1962, **59**, 232.
8. F. A. COTTON, D. M. L. GOODGAME and R. H. SODERBERG, *Inorg. Chem.* 1963, **2**, 1162.
9. A. B. P. LEVER, *Inorg. Chem.*, 1965, **4**, 1042.
10. J. GOPALAKRISHNAN, A. RAVI and C. C. PATEL, *Bull. Chem. Soc.*, 1967, **40**, 791.

Diphenylamine-Ferricyanide Couple as a *p*H Responsive System

U. MURALIKRISHNA, T. V. RAGHU RAM and Y. V. S. K. SESHA SYAI

Department of Chemistry, Andhra University, Waltair-530 003, India

Manuscript received 23 October 1979, accepted 25 December 1979

EARLIER redox indicators like ferroin, nitroferroin together with redox couples [Ce(III)-Ce(IV)] have been employed as acid-base indicators[1]. The use of diphenylamine type of compounds along with ferricyanide-ferrocyanide couple as *p*H indicators in the acid-base titrimetry for the estimation of acetic acid, benzoic acid, succinic acid, tartaric acid, oxalic acid, sulphuric acid and hydrochloric acid with sodium hydroxide is reported here.

Titration Procedure :

Aliquots of different acids (0.1 *N*) mentioned above are taken in an Erlenmeyer flask followed by 1.0 ml of the amine solution (sodium diphenylamine sulphonate in water and other amines in methanol) (0.01*M*) and 1.0 ml of potassium ferricyanide(0.1*M*). The mixture is titrated with a standard solution of sodium hydroxide (0.1 *N*) till the colour is changed from pale green to orange.

Results and Discussion

Both direct and indirect titrations can be carried out successfully. Weak bases cannot be titrated satisfactorily. However, carbonate is titratable to the first dissociation stage only. The relative percentage error and the standard deviation are shown in Table 1. The pK_{In} value obtained was 9.9. The pK_{In} value and other experimental observations were carried out using sodium diphenylamine sulphonate.

TABLE—1.

Acid	Relative Percentage error	Standard deviation
Sulphuric Acid	±0.33	0.024
Hydrochloric Acid	±0.33	0.023
Acetic Acid	±0.28	0.013
Benzoic Acid	±0.23	0.060
Oxalic Acid	±0.31	0.023
Succinic Acid	±0.28	0.060
Tartaric Acid	±0.23	0.028

The indicator action is due likely to the formation of non-protonated orange coloured oxidative form of diphenyl benzidine produced on oxidation of diphenylamine with ferricyanide in alkaline medium (>8.5 *p*H) and its conversion to the protonated green form in acid medium (<8.5 *p*H) and vice versa.

Acknowledgement

We wish to thank the U.G.C. (India) for the award of F. I. P. fellowship to T.V.R. the C.S.I.R. (India) for the award of J.R.F. to Y.V.S.K.S.S. and also to the management of M.R. College, Vizianagram for kindly deputing T.V.R. for the F.I.P.

Reference

1. E. RANCKE-MADSEN, H. SKARBYE-NIELSEN and K. OSTERGARD, *Acta Chem. Scand.*, 1954, **8**, 1414.

Studies with Chromium Ferrocyanide Epoxy Resin Based Ion-exchange Membranes

AJAY K. JAIN, SUSHMA AGRAWAL and RAJ P. SINGH

Department of Chemistry, University of Roorkee, Roorkee-247 672

Manuscript received 23 Octoer 1979, accepted 30 December 1979

INORGANIC ion exchangers have been sparsely used in the preparation of solid ion selective membrane electrodes[1,2]. The reason for limited use of these materials in the development of ion selective electrodes is that, in general, they undergo ion exchange with large number of ions and obviously electrodes based on such materials are not expected to be specific to a particular ion. However, these membrane electrodes, inspite of being not very specific to a particular ion, can be used for the estimation of ions by potentiometric titrations using the membrane as indicator electrode[3-6]. In a recent communication[7] we have reported on the use of chromium ferrocyanide membrane electrode in the potentiometric titrations of some bivalent metal ions with ferrocyanide ion. This membrane electrode though not very specific to ferrocyanide ion showed linear response to this ion in 10^{-1}-10^{-4} *M* concentration range.

Ferrocyanide ion forms stable complexes with transition metal ions and is used in quantitative analysis[8], extraction[9] and co-precipitation[10]. So in view of analytical importance of metal ferrocyanides, further titrations of some trivalent metal ions have been carried out using chromium ferrocyanide membrane as indicator electrode and results of these studies are reported in this communication.

Experimental

Potassium ferrocyanide (B.D.H. AnalaR) was used as such. All other chemicals were of analytical grade. Dilute solution of ferrocyanide was prepared by diluting 0.1*M* stock solution of potassium ferrocyanide, fresh every day.

Preparation of membranes :

The membranes were prepared by mixing 0.3 g of 'Araldite' with 0.7 g of chromium ferrocyanide[11,12] as reported earlier[7]. The membranes were equilibrated with potassium ferrocyanide solution (0.1*M*) for 15 days to generate reproducible potentials across them.

Procedure :

The equilibrated membrane was stuck to one end of 'Pyrex' glass tube, with 'Araldite'. 0.1*M* potassium ferrocyanide was taken inside this tube and the tube was placed into a 50 cm^3 beaker containing titrate solution [20 cm^3 of potassium ferrocyanide ($10^{-4}M$)]. Standard metal ion solution ($10^{-2}M$) was added from a burette and after each addition the potential of the cell.

Hg/Hg$_2$ Cl$_2$(S), KCl Sat. ‖ titrate/membrane/0.1*M* pot. ferrocyanide ‖ KCl sat., Hg$_2$Cl$_2$(S)/Hg

was measured on a Toshniwal portable potentiometer in conjunction with a sensitive suspended coil galvanometer when a steady state was reached.

Results and Discussion

Typical titration curves for Bi^{3+}, La^{3+}, Fe^{3+}, Cr^{3+} and Ce^{3+} ions are given in Fig. 1. These

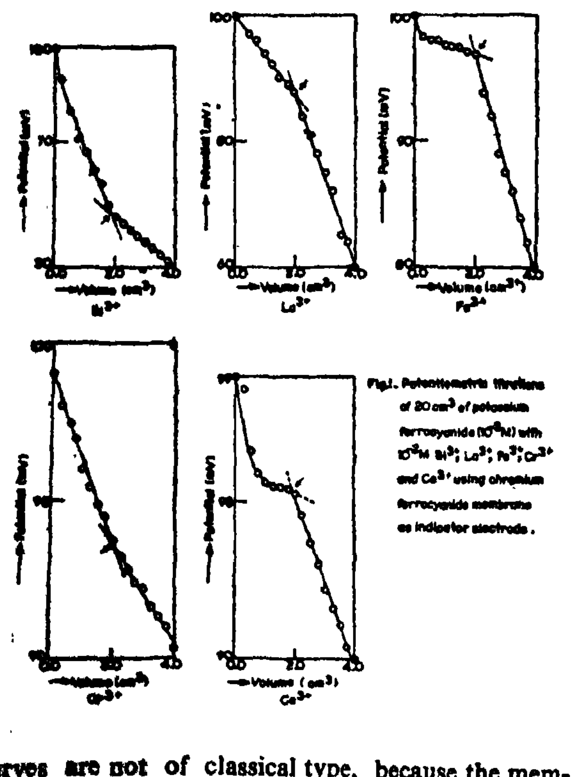


Fig. 1. Potentiometric titrations of 20 cm^3 of potassium ferrocyanide ($10^{-4}M$) with $10^{-2}M$ Bi^{3+}; La^{3+}; Fe^{3+}; Cr^{3+} and Ce^{3+} using chromium ferrocyanide membrane as indicator electrode.

curves are not of classical type, because the membrane electrode responds not only to the ferrocyanide ion[7] but also to other ions added during the titration. The different shapes of the titration curves are due to varying extent of membrane response to different ions which are added during the course of titration. However, the interference caused by other ions is not sufficient enough to mask the equivalence point. The compositions for insoluble trivalent metal ferrocyanides formed during titration is calculated from break point (shown by arrow) and is found to be KM(III)Fe(CN)$_6$. It is well known that the stoichiometry of the metal-ferrocyanide reaction depends on how the reaction is carried out and their different compositions are reported.[7,13-16]. In the studies reported here all these trivalent ions form 1 : 1 complexes and thereby making their estimation easier by titrating them against ferrocyanide.

Acknowledgement

Two of the authors (SA and RPS) are grateful to Council of Scientific and Industrial Research, New Delhi for financial assistance.

References

1. F. Helfferich, Ion Exchange, McGraw Hill, New York, 1962.
2. J. Koryta, Ion Selective Electrodes, Cambridge University Press, Cambridge, London, 1975.
3. G. J. Moody and J. D. R. Thomas, *Talanta*, 1972, **19**, 623.
4. C. J. Coetzee and A. J. Basson, *Anal. Chim. Acta*, 1971, **56**, 321.
5. C. J. Coetzee and A. J. Basson, *Anal. Chim. Acta*, 1973, **64**, 300.
6. S. K. Srivastava, A. K. Jain, S. Agrawal and R. P. Singh, *Talanta*, 1978, **25**, 157.
7. A. K. Jain, S. K. Srivastava, S. Agrawal and R. P. Singh, *Talanta*, 1978, **25**, 531.
8. G. Jander and H. Wendt, Lehrbuch der analytischen and praparativen anorganischen Chemie, Hirzel Verlag, Stuttgart, 1959.
9. V. Yatirajam and S. Dhamija, *Talanta*, 1979, **26**, 317.
10. G. B. Barton, J. L. Hepworth, E. D. Meclanhan, Jr., R. L. Moore and H. H. Van Tuyl, *Ind. Eng. Chem.*, 1958, **50**, 212.
11. W. U. Malik, S. K. Srivastava, V. M. Bhandari and S. Kumar, *J. Inorg. Nuclear Chem.*, 1976, **38**, 342.
12. W. U. Malik, S. K. Srivastava, R. P. Singh and S. Kumar, *J. Radioanal. Chem.*, 1977, **36**, 469.
13. A. Bellomo, D. De Marco and A. Casale, *Talanta*, 1972, **19**, 1236.
14. A. Bellomo, *Talanta*, 1970, **17**, 1109.
15. A. Bellomo, D. De Marco and A. Casale, *Talanta*, 1975, **22**, 197.
16. I. B. Iyer and W. H. Waggoner, *J. Inorg. Nuclear Chem.*, 1971, **33**, 721.

Residual Paramagnetism of Cobalt in Nitro-Ammine Cobalt(III) Complexes

MALATESH A. PUJAR

Department of Chemistry, Karnatak University P.G. Centre, Gulbarga-585 105, India

Manuscript received 30 April 1979, revised 7 November 1979 accepted 20 December 1979

IN continuation of our earlier work on electronic spectra, magnetic susceptibility and ^{59}Co NMR of Co(III)-ammine complexes[1-6], the study of a series of nitro-ammine Co(III) complexes is undertaken.

Experimental

All the nitro-ammine Co(III) complexes were prepared according to the known methods and then purified. The complexes were analysed for cobalt, ammonia and chloride by using standard methods. The data are found to be very satisfactory.

Physical measurements were made as described previously[3,5].

Results and Discussion

The observed chemical shifts (σ) for the complexes under investigation are given in Table 1. The values are negative since the resonance occurs at a field lower than that for the reference $K_3[Co(CN)_6]$ and shifts are quite large. It is also noted that the chemical shifts show significant differences for the complexes under study, reflecting differences in chemical (magnetic) environment between these nitro-ammine complexes.

The paramagnetic contribution (σ para) to the shielding tensor which dominates the ^{59}Co chemical shifts has been calculated for the complexes using the relation of Griffith and Orgel[7]. The observed chemical shift values have been converted to the absolute values accordingly[8].

The results of magnetic susceptibility measurements are given in Table 1. The calculation and other details of the values are given elswhere[5]. The d-d transition energy E_{dd} refers specifically to the lowest energy band ($^1A_{1g} \longrightarrow {}^1T_{1g}$).

The results (Table 1) indicate that the observed χ_m values for all the complexes are smaller than $\Sigma\chi_D$ values. The difference between the two is obviously due to residual paramagnetism χ_p due to cobalt, being called second order paramagnetism. Thus second order paramagnetic susceptibility (χ_p) for all the complexes was estimated. In NMR method, shifts of ^{59}Co are also due to second order paramagnetism which arises by mixing low lying $^1A_{1g}$ and $^1T_{1g}$ states. From this study one is inclined to believe that the much contribution to the shifts is due to the residual paramagnetism while the diamagnetic contribution has minor role in affecting σ values.

A salient feature is seen from the Table 1 that the successive replacement of NH_3 molecule by NO_2^- ion in these complexes from hexamine Co(III) results, in a decrease in the σ and χ_p values. Whereas in case of aquo, carbonato, azide and oxalato ammine series of Co(III) complexes, there is an increase in these values[1-6]. Thus, these data suggest that ^{59}Co nucleus is more shielded in nitro-ammine Co(III) complexes. Further σ and χ_p decrease with an increase in the number of nitrogroups in the coordination sphere of Co(III), which means that shielding increases with substitution of NO_2^- groups. The increase is in the following order :

Hexammine < Pentammine < Tetrammine (cis and trans) < Triammine < Diammine < Monoammine Co(III)

From the Table it is observed that few mixed ligand and few nitrito-ammine Co(III) complexes and $Na_3[Co(NO_2)_6]$ behave differently from the rest. This may be due to profound changes in the bonding,

TABLE 1—ANALYSIS, CHEMICAL SHIFT, MAGNETIC SUSCEPTIBILITY AND ELECTRONIC SPECTRAL DATA FOR NITRO-AMMINE Co(III) COMPLEXES

Complex	Observed Absolute σ % Values	Calculated σ para %	$10^6 \chi_M$	$\epsilon\chi^D$	χ^P(obs)	χ^P(caL.)	E_{dd} (cm^{-1})
1	2	3	4	5	6	7	8
1. $[Co(NH_3)_6]Cl_3$	-2.346	-2.342	63	181	118	194	21050
2. $[Co(NH_3)_5NO_2]Cl_2$	-2.281	-2.239	40	154	114	185	22030
3. $[Co(NH_3)_5ONO]Cl_2$	-2.400	-2.375	32	154	122	196	20750
4. $[Co(NH_3)_4(NO_2)_2]Cl$ Cis	-2.245	-2.204	26	127	100	182	22370
5. $[Co(NH_3)_4(NO_2)_2]Cl$ Trans	-2.218	-2.169	31	127	96	179	22730
6. $[Co(NH_3)_4(ONO)_2]Cl$ Cis	-2.428	-2.502	20	147	126	207	19760
7. $[Co(NH_3)_4H_2O(ONO)](NO_3)_2$ Cis	-2.501	-2.514	14	144	130	208	19610
8. $[Co(NH_3)_4H_2O\ NO_2](NO_3)_2$ Cis	-2.368	-2.336	30	144	114	193	21100
9. $[Co(NH_3)_4NO_2Cl]Cl$ Trans	-2.348	-2.357	19	137	118	195	20920
10. $[Co(NH_3)_3(NO_2)_3]$	-2.177	-2,144	5	100	95	177	22990
11. $[Co(NH_3)_3(NO_2)_2Cl]$	-2.249	-2.219	3	110	107	183	22220
12. $Na[Co(NH_3)_2(NO_2)_4]$	-2.152	-2.070	11	103	92	171	23810
13. $Na_2[Co(NH_3)(NO_2)_5]$	-2.140	-2.036	18	106	88	168	24210
14. $Na_3[Co(NO_2)_6]$	-2.285	-2.385	1	109	108	197	20660

reactivity of Co(III) and mixture of nitro and nitrito in the complexes.

Thus the trends in magnetic susceptibility and chemical shift values show increasing ligand filed strength as one moves down the series of complexes in Table 1. This is observed directly in the relative values of E_{dd} for complexes accordingly[7].

It is also interesting to note that the observed and calculated values in σ and χ_p are some what deviating. This may be due to some factors such as covalent bonding of ligands with Co(III), uncertainities in the values of diamagnetic susceptibilities used for evaluating terms, configurational interaction (cis and trans), the distortion in the octahedral structure of complexes of Co(III), etc. which were not considered in the theory[9,10,11].

The data σ, χ_p and E_{dd} also may be utilised very clearly to establish ligand field strength of ligands such as ONO^-, H_2O, NO_2 and NH_3, to study nitrito and nitro isomers and to distinguish cis and trans isomers in these nitro-ammine Co(III) complexes (Table 1.)

Acknowledgement

The author expresses his thanks to the authorities of TIFR, Bombay for providing NMR facilities and to Dr. V.R. Marathe for the invaluable help in getting NMR spectra and stimulating discussion.

References

1. M. A. Pujar N. S. Biradar and V. R. Marathe, 1969 35, 385.
2. M. A. Pujar and N. S. Biradar, *Z. anorg. Chem.*, 1970, 379, 88.
3. M. A. Pujar and N. S. Biradar, *J. Inorg. Nuclear Chem. Lett.*, 1971, 7, 269.
4. M. A. Pujar and N. S. Biradar, *Z. anorg. Chem.* 1972, 391, 52.
5. M. A. Pujar and N. S. Biradar, *J. Indian Chem. Soc.*, 1971, 48, 161.
6. M. A. Pujar and N. S. Biradar, *J. Karnatak Univ.*, 1970, 15, 16.
7. J. S. Griffith and L. E. Orgel, *Trans. Faraday Soc.*, 1957, 53, 601.
8. C. R. Kanekar, M. M. Dingra, V. R. Marathe and R. Nagarajan, *Chem. Phys.*, 1967, 46, 2009.
9. N. A. Matwiyoff and W. E. Wayman, *Inorg. Chem. Acta.* 1970, 4, 460.
10. S. Fujiwara, F. Yajima and A. Yamavki, *J. Mag. Resonance*, 1969, 1, 203.
11. C. P. Bettridge and R. M. Golding, *J. Chem. Phys.*, 1969, 31, 2197.

Extraction of Manganese(II) with Salicylaldoxime—Synergic Effect of Pyridine*

P. B. SANKARA REDDY** and S. BRAHMAJI RAO

Department of Chemistry, SVU Autonomous Post-Graduate Centre, Anantapur-515 003, India.

Manuscript received 30 July 1979, accepted 30 December 1979

OXIMES (mono and di) of carbonyl compounds are extensively employed as extraction photometric reagents for many metal ions.[1]. A survey of literature has shown that very little work on oximes for extraction photometric determination of manganese(II) is reported. Flagg and Furman[2] reported that salicylaldoxime reacts with many metal ions including manganese. However no work was reported on the extraction photometry of manganese with this oxime. Gorbach *et al.*[3] made casual mention about the possible extraction of manganese with salicylaldoxime with chloroform. The present authors observed that the oximate complex of manganese(II) formed in alkaline solutions is quantitatively extractable into *n*-butanol. However the yellowish brown colour of the butanolic layer was unstable and deepened with time, even though the determination of the metal ion[4] was possible, if the measurements are completed within 30 minutes. It is found from the literature[5] that this phenomenon of colour change is a common occurance due to aerial oxidation of Mn(II) and addition of pyridine was suggested to over come this difficulty. Present authors however noticed that the colour of *n*-butanolic layer was unstable even after the addition of pyridine. In contrast to the behaviour in *n*-butanol, the metal is extracted completely into toluene in presence of pyridine. The colour was also stable for long times. There is negligible extraction into toluene in the absence of pyridine. The organic layer is colourless, if the extraction is carried out without salicylaldoxime. Extraction photometric study of Mn(II) with salicylaldoxime into toluene in presence of pyridine is therefore carried out and the results are communicated herewith.

The studies pertaining to the effect of *p*H on the reaction between Mn(II) and the oxime revealed that there is yellow colour formation in the range 8-10. The soluble coloured complex was extracted into toluene in presence of pyridine. The absorbance of the organic phase obtained at *p*H 10 measured against the solvent blank showed highest value at 420 nm in the visible range (400-700 nm). The absorbance is constant for several weeks. The aqueous phase after extraction showed zero absorbance. Chemical examination of the aqueous phase showed that a quantitative recovery is achieved when the concentration of the oxime is atleast 20 fold excess and pyridine is 5% in the organic phase.

*Presented at Annual Convention of Chemists, Andhra University, Waltair, India (1978).

**Department of Chemistry, Government College (Men), Cuddapah-516 004, India.

Recommended Procedure

5 ml of ammonia-ammonium chloride buffer (*p*H adjusted to 10), 1 ml of sodium perchlorate (1 *M*), 1 ml of the oxime solution ($10^{-2}M$), 0.5 ml pyridine and different aliquots of $MnSO_4$ solution ($10^{-3}M$) are taken in a 25 ml separatory funnel. The volume of the aqueous phase is maintained at 10 ml by adding requisite volume of distilled water, 10 ml of toluene is added to the contents of the funnel and shaken well, for five minutes. After equilibration, the organic layer is separated, dried over anhydrous sodium sulphate and the absorbance measured against solvent blank at 420 nm. The organic phase obtained in the extraction carried out without the metal ion is used as the solvent blank. The good linear plot obtained between the amount of the metal ion and the absorbance showed that manganese can be estimated by the present method accurately in the range 0-6 μg/ml. The molar absorptivity (ϵ) and the Sandell sensitivity (S) at 420 nm are 0.58×10^4 lit. $mole^{-1}\ cm^{-1}$ and 0.0095 $\mu g/cm^2$ respectively. The standard deviation is 0.005. Zn(II) and Ni(II) do not interfere. More than 2 fold excess of Fe(III) interferes in the determination.

The Coleman[6] graphical analysis of the organic layer showed that only a single species is responsible for the colour of the organic phase. Absorbance of the toluene layer increased with increase of pyridine upto 5% and later remains constant.

Acknowledgement

The authors wish to thank the Director, SVU Autonomous Post-Graduate Centre, Anantapur, India for providing necessary facilities. One of the authors (PBS) gratefully acknowledges the award of Teacher Research Fellowship by University Grants Commission and to the Director of Higher Education, Government of Andhra Pradesh for deputation.

References

1. A. K. De, S. M. Khopkar and R. A. Chalmers, "Solvent Extraction of Metals", Van Nostrand Reinhold, London 1970.
2. John F. Flagg and Howell Furman, *Ind. Eng. Chem., Anal. Ed.*, 1940, **12**, 529.
3. G. Gorbach and F. Pohl, *Microchemie*, 1951, **38**, 258.
4. P. B. Sankara Reddy and S. Brahmaji Rao, *Curr. Sci.*, 1978, **47**, 84.
5. Z. Marczenko and M. Mojski, *Chem. Anal.* (Warsaw), 1971, **16**, 865.
6. J. S. Colemyn, L. P. Varga and S. H. Mastin, *Inorg. Chem.*, 1970, **9**, 1015.

Thermal Studies of Absorption Behaviour of Some Organic Compounds on Partially Co(II) and Ni(II)-Exchanged AW500 Zeolites

MADHU BHAI BHATT and SATI PRASAD BANERJEE*

Department of Chemistry, University of Saugar, Sagar 470 003, M.P.

Manuscript received 21 August 1979, accepted 30 December 1979

PARTIALLY cation-exchanged samples of synthetic zeolite AW500 were prepared with cobalt (II) chloride-hexahydrate and nickel(II) chloride-hexahydrate. Thermal behaviours of these zeolites after interaction with pyridine, triethanol amine, trichloroethylene and 1, 1, 2, 2-*tetrachloroethane* have been investigated by thermogravimetry, differential thermal analysis and differential thermogravimetry. Experimental details and the thermal behaviours of these exchanged samples along with data on absorbed samples of partially-exchanged Cu(II) and Hg(II)-AW500 with these organic compounds have been communicated earlier[1-3]. The thermal data obtained with the absorbed samples of Ni(II)-and Co(II)-AW500 zeolites have been tabulated (Table 1).

Results and Discussion

Complex formation reactions of pyridine and its derivatives with both cobalt(II) and nickel(II) compounds have been studied by several workers[4-7]. Cobalt(II) was found to give a chelate with triethanolamine where the ligand was tetradentate giving a trigonal bipyramidal cofiguration around the metal atom[8]. Nickel(II) on the other hand formed a polycondensed complex with the ligand[9].

Infrared spectroscopic studies of pyridine adsorption on a series of oxide surfaces, mainly chemically modified SiO_2, showed that two types of Lewis acid centres were formed differing in the coordination of the exposed central atoms at the surface Among the bonds formed during adsorption, the coordinate bond of pyridine on electron acceptor centres of surface mixed oxides of SiO_2 was the strongest[10]. The same authors[11] reported the appearance of a broad, relatively weak band at $\sim 2700 cm^{-1}$ due to pyridine absorption on various siliceous surfaces. The band was assigned to the $N^+—H$ stretching vibration of pyridinium ions.

In the present study involving pyridine absorption no clear indication of the nature of interaction is available as neither the temperature of water elimination nor the pattern of thermal decomposition reliably indicates structure or bonding[12]. Absorption of triethanolamine on the zeolites to a considerable extent is however indicated by the presence of an unusually strong exothermic peak in the

TABLE 1—THERMAL DATA OF ZEOLITE SAMPLES

	Zeolite	DTA Endotherm °C	DTA Exotherm °C	TGA Weight Loss %
1.	Pyridine absorbed-Co(II)-AW500	100, 220, 500 (shallow)	420 (undefined), 540, 780	17 (Two-step)
2.	Triethanolamine absorbed Co(II)-AW500	120, 400	300 (shoulder), 360, 460, 760	35 (Three-step)
3.	Trichloroethylene absorbed Co(II)-AW500	220, 540 (undefined)	380, 550 (shoulder), 800	16 (Two-step)
4.	1,1,2,2-Tetrachloro-ethane absorbed Co(II)-AW500	100, 220, 500 (shallow)	440 (shoulder), 550, 780	18 (Two-step)
5.	Pyridine absorbed-Ni(II)-zeolite	100, 200	400 (shoulder), 480 (hump) 540 (shoulder), 800 (shoulder)	20 (Two-step)
6.	Triethanolamine absorbed Ni(II)-AW500	120	360 (shoulder), 440, 800	35 (Three-step)
7.	Trichloroethylene absorbed Ni(II)-AW500	100 (undefined), 220	360, 580, (hump), 780 (shoulder)	17 (Two-step)
8.	1,1,2,2-Tetrachloro-ethane absorbed Ni(II)-AW500	100, 220	480, 580, 800 (shoulder)	18 (Two-step)

DTA curve and atleast 3-step weight loss in the TGA curve. But though complex formation is the possible interaction with the zeolites for both pyridine and triethanolamine, the thermal data obtained especially with the former, cannot fully confirm this.

Studies of sigma and pi-bond interactions on the zeolite surface were undertaken with the adsorption of ethane and ethylene on the cation-exchanged forms of zeolite X[13]. Formation of charge transfer complex due to adsorption of tetracyanoethylene onto dehydrated 13X has also been reported[14]. Similar reactions are therefore possible involving trichloroethylene and 1, 1, 2, 2-tetrachloroethane on Co(II)-and Ni(II)-exchanged AW500. However, the TGA data of these absorbed samples indicate very low absorption confirming the findings of Lukin *et al*.[15] that zeolites having binders exhibit lower absoption compared to zeolite crystals.

Loss of weight for the zeolite samples is a two-step one except for triethanolamine absorbed samples. For two-step weight loss a faster rate of evolution occurs upto about 200° and a slower rate beyond it. Desorption studies of various substances from zeolites show that dehydration of NaA occurs in two stages, a fast evolution around 100° and a slow evolution at about 300°[16]. The triethanolamine absorbed samples of Co(II)-and Ni(II) lose weight in three distinct steps. The rates of loss upto 200° and beyond 300° are slower compared to the rate between 200 and 300° when triethanolamine is desorbed. The other two steps are for dehydration with a maximum rate of loss around 100°. A total weight loss of about 35% is obtained after complete desorption. This figure is much higher than weight losses obtained for other zeolite samples.

The DTA endotherms around 100 and 220° are due to dehydration and beyond 220 occurs desorption of absorbed molecules. These endotherms are mostly shallow and not clearly defined due to very low absorption. Exothermic effects at lower temperatures are for oxidation of the organic molecules while the peaks around 800° indicate thermal stability of zeolite structures. These exotherms are mostly hump-like peaks with the exception of triethanolamine absorbed zeolites which exhibit very strong oxidation peaks around 450°.

Acknowledgement

We are thankful to the Union Carbide Corporation, U.S.A., for the gift sample of zeolite AW500 in 1/16" pellet form (Lot No. 5942940026). One of us (M.B) thanks the U.G.C. for awarding a Junior Research Fellowship to him.

References

1. B. K. CHAPRA and S. P. BANERJEE, *J. Therm. Anal.*, Communicated, 1979.
2. MADHU BHAI BHATT and SATI PRASAD BANERJEE, *J. Therm. Anal.*, Communicated, 1979. (in press).
3. MADHU BHAI BHATT and SATI PRASAD BANERJEE, *Indian J. Chem.*, 1979. (in press).
4. R. J. H. CLARK and C. S. WILLIAMS, *Inorg. Chem.*, 1965, 4, 350.
5. MARIA TERESA PEREIRA LEITE, *Rev. Port. Quim.*, 1974, 16, 21.
6. E. M. KHAIRY, M. M. KHATER and A. F. SHOUKRY, *Egypt J. Chem.*, 1975, 18, 1017.
7. M. S. BARVINOK and A. V. PANIN, *Zh. Neorg. Khim.*, 1978, 23, 2442.
8. V. N. EVREEV, A. P. BOGDANOV, V. A. GOLUB, V. V. ZELENTSOV, I. I. OLIKOV and V. N. SHAPRANSKII, *Koord. Khim.*, 1978, 4, 260.
9. SARRION MARTINEZ, LUISA MARIA and DANIEL B. PORTER, *Ion*, 1976, 36, 581.
10. WALTER POHLE and PETER FINK, *Z. Phys. Chem.*, 1978, 109, 77.
11. WALTER POHLE and PETER FINK, *Z. Phys. Chem.*, 1978, 109, 205.
12. R. H. NUTTAL and D. M. STALKER, *J. Inorg. Nuclear Chem.*, 1978, 40, 39.
13. A. G. BEZUS, A. V. KIZELEV, Z. SEDLACEK and PHAM QUANG DU, *Trans. Faraday Soc.*, 1971, 67, 468.
14. P. TABOURIER and C. DRUON, *C. R. Academic Science, Paris, Series C*, 1973, 79, 1425.
15. V. D. LUKIN, V. A. ASTAKHOV, P. G. ROMAOKOV, G. T. YUR'EVA and T. I. PRYAMUSHKO, *Zh. Prik. Khim.*, 1974, 47, 460.
16. V. A. ASTAKHOV, L. A. MEERSON and G. S. KLYUSHKOVA, *Vestsi Akad. Nauk BSSR, Ser, Khim.*, 1978, 3, 118.

Colorimetric Determination of Resorcinol in Pharmaceutical Preparations

R. T. SANE* and C. H. THOMBARE

Department of Chemistry, Ramnarain Ruia College. Matunga, Bombay-19

Manuscript received 12 October 1979, accepted 30 December 1979

1-3 dihydroxybenzene commercially known as resorcinol is a fungicide. It is used to cure some skin deceases due to its antifungal and antibacterial activity. Resorcinol is formulated in pharmaceutical preparations in the form of ointments, lotions and creams for external application. Literature survey reveals many colorimetric and titrimetric methods of estimation of resorcinol.

The official method[1] involves iodometric titration. Colorimetric methods using Felin-Denis reagent[2], 4-dimethylaminobenzaldehyde[3], vanadates of 8-hydroxyquinoline[4] are lengthy as complete colour development takes about 30 minutes. Colour formation with iron salts[5] and 3, 5-dibromo *p*-benzoquinonechlorimine[6] are non-specific as all the phenolic compounds develop colours with these reagents. We have observed that, resorcinol forms violet colouration with *p*-aminophenol (PAP) in alkaline medium. This colour reaction was studied and standard procedure for estimation of resorcinol was developed.

It was found that this procedure requires only 5 minutes for complete colour development and it does not involve any special treatment as required in the other published methods[2-6].

Experimental

All chemicals and solvents used were of A.R. grade.

Reagent solution :

0.04 percent solution of PAP was prepared by dissolving 40 mg of PAP in 100 ml ethanol.

Alkali solution :

1 *M* NaOH was prepared in distilled water.

Standard solution of resorcinol :

A standard solution of resorcinol of concentration 1 mg/ml was prepared in distilled water and working standard solution of concentration 10 μg/ml was prepared from this stock solution.

Sample solution of resorcinol :

The sample solution of concentration 10 μg/ml of resorcinol was prepared in distilled water.

Assay procedure :

2 ml of each standard and sample were taken separately in 10 ml test tubes and 2 ml of 1 *M* NaOH and 1.4 ml of the reagent were added. The volume of the mixture was adjusted to the mark wish distilled water. After 5 minutes the absorbance was noted at 585 nm against the reagent blank.

Table 1 gives the comparative data of the application of the proposed method in the estimation of resorcinol in the commercial pharmaceutical products.

Results end Discussion

The proposed method is simple, fast and accurate. The results obtained are reproducible and compare satisfactorily with those obtained from the official method. Commonly used bases in creams, lotions and ointments like lanolin, kaolin, white parafin base etc. produce no difficulty in estimation. Other commonly formulated ingredients like cetrimide, boric acid, iodochlorohydroxyquinoline etc. do not interfere. The percentage recovery is almost 100.

TABLE—1

Product	Resorcinol present.	Resorcinol found.	Percentage recovery.	Resorcinol found by official method[1]
Ointment-A (Bismuth Resorcin Compound)	1.75 %	1.75 %	99.80	1.80 %
Cream-A (Resorcinol.)	3 %	2.98 %	99.78	2.90%
Lotion-A (Resorcinol.)	3 %	3.01 %	100.06	2.90%

References

1. The British Pharmacopoeia, London, Pharmaceutical Press, 1973, p. 412.
2. J. HALMEKOSKI, (Inst. Chem. Helsinki), *Suomen Kem.* 1959, 32, 274.
3. P. LOZSA (Orszagos Kozegeszmeguggi Intezet Kem. Osztailya, Budapest, Hungary) *Acta. Pharm. Hung.*, 1967, 37, 145.
4. I. M. KORENMAN, V. G. GANINA and M. V. KURINA, *Trudy Khim., Khim. Tekhnol* (*Gor'kii*), 1968, 2, 140.
5. EIJIRO KAMATA (Lab. of Anal. Chem. Nagoya Univ. Chikusa-Ka, Japan), *Bull. Chem. Soc., Japan*, 1964, 37, 1674.
6. V. DAS GUPTA, (Coll. Pharm., Univ. Houston, Tex 77004, USA), *J. Pharm. Sci.*, 1976, 65, 144.

10, 10-Dimethyl hexacosan-7 one from *Euphorbia heterophylla* Linn.

K. P. TIWARI, P. KUMAR and M. MASOOD

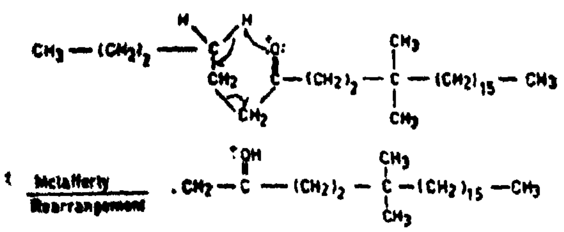
Department of Chemistry, University of Allahabad, Allahabad, India

Manuscript received 2 January 1979, revised 21 August 1979, accepted 23 November 1979

Euphorbia heterophylla Linn. (Euphorbiaceae) is an ornamental plant commonly known as Mexican-Fire Plant. It is widely distributed in tropical America, Texas, Western Himalayas and West Bengal[1]. The present communication deals with the isolation of a new aliphatic ketone from petroleum ether extract of the leaves of *E. heterophylla*.

Study of 10, 10-dimethyl hexacosan-7 one :

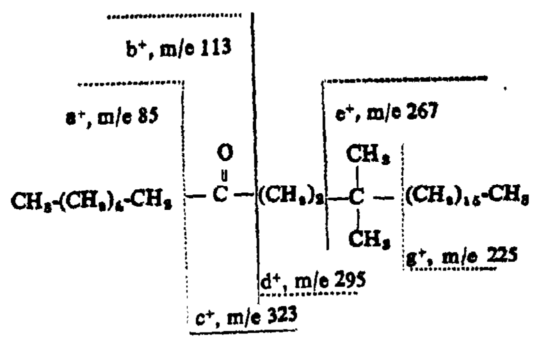
The compound, $C_{28}H_{56}O$, m/e 390 ($M^+ - H_2O$), m.p. 76–77°, ν_{max}^{KBr} 2857, 2778, 1456, 730, 718 cm^{-1} (aliphatic long chain), 1718 cm^{-1} (carbonyl group) and 2292, 1372, 928 cm^{-1} (C–C(C)(C)–C type branching),[2,3,4] NMR ($CDCl_3$) δ 0.90 (s, 12H, 4C–CH_3 groups), δ 1.27 (s, 36H, 18–CH_2 groups), δ 1.78 (s, 4H, 2 CH_2 groups β to>C=O groups), δ 2.34 (s, 4H, 2CH_2 groups α to>C=O group), formed DNPH derivative, m. p. 90°, gave a hydroxy compound, $C_{28}H_{58}O$, m.p. 65–67°, ν_{max}^{KBr} 3226 cm^{-1} (broad hump, hydroxyl group) on $LiAlH_4$ reduction indicating it to be a long chain aliphatic ketone. The presence of 2 methylene groups adjacent to carbonyl group and 2 methylene groups β to>C=O group showed the absence of branching at α and β carbons with respect to <C=O group. Identification of *n*-hexanoic acid and *n*-heptanoic acid in the mixture of fatty acids obtained after $KMnO_4$ oxidation of the compound, indicates the straight chain nature of smaller alkyl group having 5 or 6 carbon atoms. The structure of the ketone has been elucidated by the study of mass fragmentation pattern of the ketone[5-8] as shown in Table 1.



f^+, m/e 338

The mass spectrum does not show the molecular ion peak at m/e 408, instead a peak at m/e 390 (due to loss of H_2O molecule from the M^+ ion) is observed. The other significant peaks appeared at 338 (f^+, 26), 323 (c^+, 30), 295 (d^+, 55), 267 (e^+, 55), 252 (h^+, $e^+ - CH_3$, 40), 225 (g^+, 23), 211 (i^+, $g^+ - CH_2$, 42), 113 (b^+, 76), 85 (a^+, 100), 71 ($a^+ - CH_2$, 58), 57 ($a^+ - 2CH_2$, 67), 43 ($a^+ - 3CH_2$, 72), 29 ($a^+ - 4CH_2$, 52).

TABLE—1



10, 10-Dimethyl hexacosan-7 one

Experimental

Isolation of 10, 10-Dimethyl-hexacosan-7-one :

The air dried, powdered leaves (3 kg) of *E. heterophylla* (supplied by M/s. United Chemical and Allied Products, Calcutta) were extracted with pet. ether in a soxhlet extractor. The extract was concentrated under reduced pressure and kept overnight whereupon a deposit (5 kg) was obtained. The deposit was separated dissolved in benzene and chromatographed over neutral alumina. Elutions with pet. ether yielded only waxy material while elutions with pet. ether : benzene (1 : 1 v/v) mixture yielded a solid (3.5 g) which was dissolved in hot pet. ether and left overnight at room temperature. The solid so obtained was separated by filtration and crystallised from $CHCl_3$: MeOH mixture to yield 10, 10-dimethyl-hexacosan-7-one (3.1 g) as prisms, m.p. 76-77°, found C, 82.31, H, 13.80 per cent, calculated for $C_{28}H_{56}O$, C, 82.35 and H, 13.72 per cent.

$LiAlH_4$ reduction of 10, 10-dimethyl-hexacosan-7 one :

$LiAlH_4$ (200 mg) was added to a suspension of the compound (200 mg) in anhydrous THF (30 ml) in a flask equipped with a reflux condenser fitted with a $CaCl_2$-guard tube. The mixture was refluxed for 5-6 hrs and was allowed to stand overnight. The excess of $LiAlH_4$ was decomposed by the cautious addition of cold water. Working up in the usual way yielded a hydroxy compound, $C_{28}H_{58}O$, m.p. 65-67°.

$KMnO_4$ oxidation of 10,10-dimethyl-hexacosan-7 one :

The ketone (2.6 g) was dissolved in acetone (10 ml) and 5 ml each of 10% aqueous NaOH and 5% aqueous $KMnO_4$ solutions were added. The mixture was refluxed for 6 hrs. On working up in the usual

way a mixture of fatty acids was obtained. The chromatographic examination of the mixture of fatty acids revealed the presence of *n*-hexanoic acid and *n*-heptanoic acid.

Acknowledgement

The authors are grateful to Dr. D.S. Bhakuni (Central Drug Research Institute, Lucknow), Dr. T.R. Govindachari (CIBA-GEIGY Research Centre, Bombay) and Dr. D.H. Williams (Stanford University) for recording spectral data of the compound reported in this paper.

References

1. H. H. HAINES, 'Botany of Bihar and Orissa' Adlard Sons and West Newman Ltd., London. 1925, 144.
2. H. W. THOMPSON and P. TORTINGTON, *Trans. Faraday Soc.*, 1945, 41, 246.
3. H. E. KHADEM and M. M. A. RAHMAN, *J. Chem. Soc.*, 1965, 3488.
4. L. A. JONES, J. C. HOLMES and R. B. SELIGMAN, *Anal. Chem.*, 1956, 28, 81.
5. N.H. ADRIAN and D.H. WILLIAMS, *Org. Mass. Spectrum*, 1969, 2, 331.
6. R. M. SILVERSTEIN and G. C. BASSLER, 'Spectrometric Identification of Organic Compounds', John Wiley & Sons, London, ed. 1967, p. 19.
7. H. BUDZIKIEWICZ, C. DJERASSI and D. H. Williams, 'Mass spectrometry of Organic Compounds', Holden-Day, San Francisco, 1967, (a) p. 134 ; (b) p. 138.
8. F. W. MCLAFFERTY, 'Introduction of Mass Spectra', W. A. Benjamin, Inc., New York, 1967, p. 185.

J. Indian Chem. Soc.,
Vol. LVII, March 1980, pp. 352

OBITUARY

Professor V. Pandu Ranga Rao

(1929-1980)

It is with deep sense of sorrow we record the sad and untimely demise of Professor V. Pandu Ranga Rao, Head of the Department of Chemistry and Principal, University College, Nagarjuna University, Guntur, on February 2, 1980.

Born in 1929, in Vinukonda in Guntur District, Professor Pandu Ranga Rao had his education in the Hindu College, Guntur and the University Colleges, Waltair. He worked in the laboratories of Professor G. Gopala Rao and obtained his doctorate degree in 1956. He joined the Chemistry Faculty of the University Colleges, Waltair in 1955 and rose to the position of Reader in 1959. He moved to the then Andhra University Post-graduate Centre, at Guntur in 1968 as Professor and Head of the Department of Chemistry. He became the Principal of the Nagarjuna University College in 1979.



Professor Pandu Ranga Rao's research contributions in the field of solvent extraction with reference to synergism, ternary complex formation and trace metal analysis have won him national and international recognition. As many as 17 candidates have taken their doctoral degrees under his guidance and he had nearly 100 research publications to his credit. He was intimately associated with the Andhra Pradesh Telugu Akademi in the preparation of chemistry text-books in Telugu language. He served on various academic bodies of several universities and was a Fellow of the Andhra Pradesh Akademy of Sciences.

His suave temperament, simple and unassuming nature, dedication to academic activity and intellectual honesty have won for Professor Pandu Ranga Rao great admiration from his colleagues, friends and students.

The community of chemists are poorer by his death at a time when greater and richer research contributions were expected of him.

He leaves behind his wife, two sons and daughter, and large circle of students, and friends to bemoan his loss.

May his Soul rest in peace.

U. Murali Krishna

AUTHOR INDEX

INFORMATION FOR AUTHORS OF CONTRIBUTIONS AND PUBLISHERS OF BOOKS

1. **Manuscripts for publication** in the *Journal of the Indian Chemical Society* should be typed with double spacing on one side of good quality paper with at least 3.5 cm margin on the left hand side and clear margin on all other sides; ***the original and 2 carbon copies are to be submitted.* These should be addressed to the Honorary Editor, Indian Chemical Society, 92, Acharya Prafulla Chandra Road, Calcutta-700 009.**

On the top right hand corner of the title page of the manuscript, the **section** (viz. Inorganic Chemistry, Physical Chemistry, Organic Chemistry, Analytical Chemistry, Biochemistry, Industrial Chemistry/Chemical Engineering, etc.) for which the communication is to be considered **should be clearly indicated.**

On receipt of a paper the author sending the paper shall be duly intimated of the Society's registration number for the manuscript which must be quoted by the author in all future correspondence on it to the Society. *All such future correspondence should be addressed to the* **Executive Editor.**

2. **A paper will not be accepted for publication unless the author or at least one of the authors (in case of a contribution submitted jointly by more than one author) is a Fellow or a Member of the Indian Chemical Society of some category.**

3. Original contributions to new chemical knowledge, both experimental and theoretical, in all the areas of Chemistry, are accepted for publication in the *Journal of the Indian Chemical Society.* Two types of contributions are considered for publication: *Articles* and *Notes.* Both categories should have sufficient information to permit repetition of the experimental work.

Contributions which have been published or accepted for publication in another journal or in any other freely available printed work **will not be published** in the *Journal of the Indiun Chemical Society.* **A declaration to that effect from the author must accompany a manuscript submitted for publication.**

Authors are solely responsible for the factual accuracy of their contribution.

4. A prospective contributor should consult recent issues of this journal to get acquainted with its *contents* and *style.* Definitive accounts of significant completed studies presenting new important data or providing a fresh approach to an established subject should be submitted as **articles.** The presentation should be in a logical manner consistent with accuracy, clarity and brevity. The text should be divided into the following sections: (a) Introduction; (b) Experimental; (c) Results and Discussion; (d) References. Divisions within the sections should be indicated by sub-headings. **Extensive review and unnecessary details of earlier work should be avoided.** Well known or previously published procedures followed in the experimental work should only be referred to omitting details. Important findings and results of much interest which may require priority in publication shall be considered for publication as **notes.**

Any portion of the text for which a special type of print is required must be indicated: **single underlining** for *italic* type and **double underlining** for *bold black* type.

The *title* of a contribution should tell accurately and clearly what the paper is about. The first letter of each noun and adjective in the title must be in *capital.* The title must be followed by the names of the authors and their addresses. The name of the senior author to whom correspondence may be made about the paper must be marked by an asterisk (*). His present address, if different from that quoted as above, must be given in a foot-note.

Every article must be accompanied by an informative *abstract* that summarizes the principal findings of the work presented in the paper. Normally it should not be over 3 per cent. of the length of the paper and should not exceed 250 words. It should be in a form that it may be used directly for publication in abstracting periodicals. This abstract should be typed before the main text and indented ca. 2 cm to the right of it. *No such abstract is necessary for notes.*

5. The charge carried by an ion should be indicated in the following manner: Na^+, Cu^{2+}, $Co(NH_3)_6^{3+}$ Cl^-, SO_4^{2-}, $Fe(CN)_6^{3-}$, etc. Standard abbreviations should be used throughout the experimental section: e.g., m.p., b.p., sec, min, hr, mg, g, kg, mm, cm, cps, tlc, uv, ir, nm, etc. Analytical

results should be reported in the form : (Found : N,. ...; Cl...... ; Ni,...... per cent. Calcd. for...... N,...... ; Cl,...... ; Ni,...... per cent.).

6. *Literature citations* should be numbered consecutively and these numbers are to appear as superscripts in appropriate positions in the text. Care must be exercised for uniformity in reference citations. "Ibid", "Idem", "et al", etc. should not be used. *Abbreviations for titles of journals must ordinarily conform to those used by the "Chemical Abstracts" published by the American Chemical Society (vide : "List of Periodical Abstracted").* **All the references must be typed in their serial order at the end of the text in the manuscript. The names (not surnames only) of all the authors should be given.** A few sample citations are noted below :

1. P. C. Ray, *J. Indian Chem. Soc.*, 1924, **1**, 207.
2. R. J. Kula, D. T. Sawyer, S. I. Chan and C. M. Finley, *J. Amer. Chem. Soc.*, 1963, **85**, 2930.
3. C. S. Garner and D. A. House in "Transition Metal Chemistry", (Ed.) R. L. Carlin, Marcel Dekker, New York, 1970, Vol 6, p. 59.

Foot-notes must be referred to in the text with suitable symbols such as,*, †, ‡, §, ‖, etc.

7. **Instructions for Diagrams and Figures.** The number of tables, diagrams and photographs should not be more than what is absolutely necessary, in view of the fact that the reproduction of such materials is very costly. **If these exceed 20% of the pages of the text, authors may be asked to pay for the excess cost.**

a. Figures should be numbered with Roman numerals and mentioned consecutively in the text indicating their respective locations. *All Figures must have legends and these should be typed out separately in a sheet of paper at the end of the main text of the manuscript.* **Legends should not duplicate information in the text.**

b. One set of the drawings should be made with India ink on tracing cloth or good quality white drawing paper. *Gragh paper should not be used.* Lines should contrast sharply with the background. **Most drawings should be planned for reproduction to a column width of 7.5 cm. Lettering should be large enough to be 1.5 mm high after reduction.** Large drawings should be simplified, for submitting with the manuscript, in a size which is reducible to not more than 16 cm × 22 cm. For satisfactory reproduction all drawings should be approximately twice the size in which they are to appear in the print. Use of legends in the body of the diagram must be reduced to the minimum. Free hand drawings and drawings unsuitable for block making cannot be accepted. If necessary the Editors may get the figures redrawn properly for which the actual cost is to be borne by the author(s). Structures and formulae which cannot be composed must also be submitted as suitable drawings for blockmaking.

c. If original tracings are not available, glossy prints of the tracings can be used if the background is clear and the lines are distinct.

d. Photographs should be glossy black and white prints with sharp contrast. Paper clips mark the surface, and writing on the back of photos often punches through, spoiling the prints. **Photographs of equipment should be avoided.** Photomicrographs should be unmounted and should not be more than 7.5 cm. wide.

8. *Reprints* shall be supplied only on receipt of payment of the usual charges. i.e. 50 reprints @ Rs 10/- per page or part thereof, subject to a minimum charge of Rs 25/- ; 100 reprints of 1—2 pages @ Rs. 50/- and for subsequent 2 pages or part thereof @ Rs 40/- next 100 reprints or part thereof at half the original rate. *No free reprints are supplied and no such request can be entertained.* Reprint order form is sent to author with the proof.

9. **Books submitted for review** in the *Journal of the Indian Chemical Society* must be sent in **duplicate** to the Honorary Editor, Indian Chemical Society, 92, Acharya Prafulla Chandra Road, **Calcutta-700 009, so that one copy may be retained in the Library of the Indian Chemical Society, while the other copy may be retained by the reviewer for his personal use.**

In case of rejection of a paper, the opinion of the Honorary Editor shall ordinarily be treated as final.

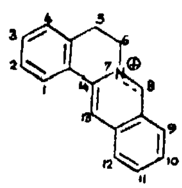
J. Indian Chem. Soc.,
Vol. LVII, April 1980, pp. 353-358

Protoberberine Alkaloids*

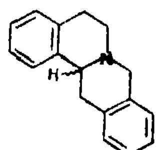
T. R. GOVINDACHARI**

I am greatly honoured for having been asked to deliver the Acharya J. C. Ghosh Memorial lecture. Acharya Ghosh was one of India's great scientists who laid the foundations for scientific research and education in our country. We of the present generation owe a debt of gratitude to Acharya Ghosh for his great service in the cause of science.

The protoberberines are an interesting group of alkaloids which commonly occur in plants belonging to the *Berberidaceae*, *Ranunculaceae*, *Menispermaceae* and *Rutaceae*. The first alkaloid of the series berberine was isolated in 1837 from *Berberis vulgaris* and now over one hundred alkaloids are known. The alkaloids occur both in the form of quaternary salts with the skeletal structure I or as tertiary bases of type II.



I

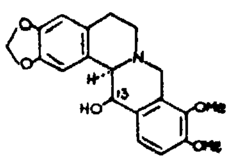


II

There are several excellent reviews of protoberberine chemistry[1-4]. In this lecture attention will be confined mainly to some interesting contributions made from Presidency College, Madras, in the field of protoberberine chemistry.

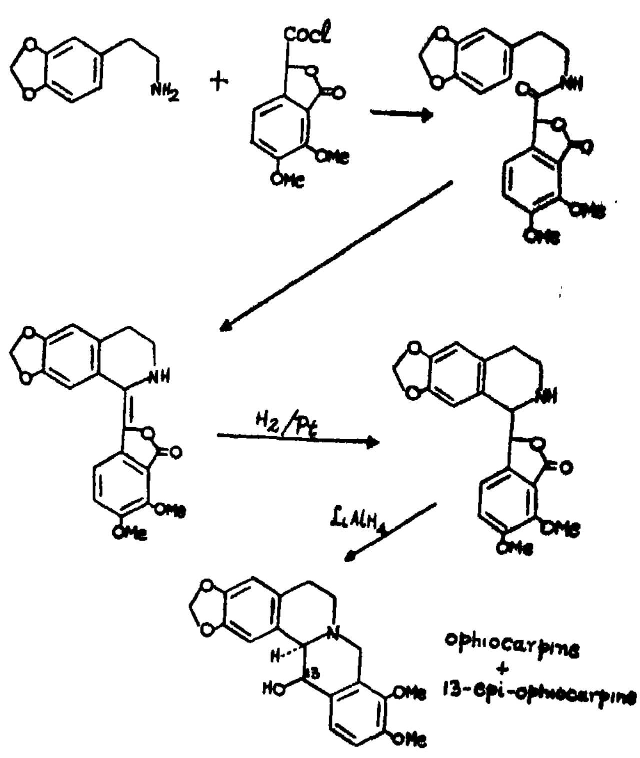
Synthetic studies :

The alkaloid ophiocarpine(III) is unusual in that, it carries an alcoholic hydroxyl group at C_{13}. Its synthesis was effected as depicted in Scheme I[5] based on a synthetic route devised by Perkin *et al*[6].



III

Chart -1

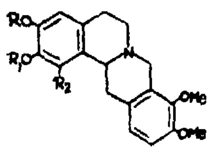


The meconin carboxylic acid needed in the synthesis was easily made from opianic acid obtained by oxidation from narcotine, the most abundant alkaloid of opium. The diastereoisomeric mixture of dl-ophiocarpine and dl-epi-ophiocarpine was separated and the former resolved yielding l-ophiocarpine identical with the natural product.

Hydrogenolysis of d-ophiocarpine yields l-tetrahydroberberine, establishing the configuration at C_{14} as (R)[7]. Since both ophiocarpine and epiophiocarpine show Bohlmann bands, both should have a trans-quinolizidine ring system. Ophiocarpine has OH absorption in the infrared, characteristic of strong intramolecular hydrogen bonding, possible only if the OH is axial. This leads to the absolute configuration depicted in III[7].

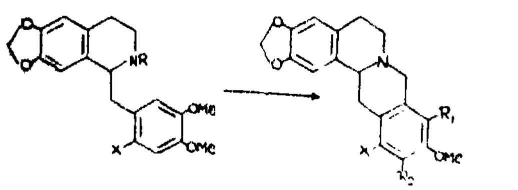
* Acharya J. C. Ghosh Memorial lecture delivered on November 9, 1979 at Madras.
** Director, Research & Development, Amrutanjan Ltd. Madras-4

The benzylic hydroxyl at C_{13} is easily removed by hydrogenolysis. The route depicted in Chart I was employed for the syntheses of dl-capaurimine (IV)[8], as well as for the phenolic alkaloids corypalmine(V) and isocorypalmine(VI)[9]. The last step was a reduction effected with a Pd catalyst in the presence of perchloric acid.



IV R = R_1 = Me ; R_2 = OMe
V R = H ; R_1 = Me ; R_2 = H
VI R = Me ; R_1 = H ; R_2 = H

The method can be used for a large number of protoberberine alkaloids, most of which carry methoxyl groups at C_9 and C_{10}. Since meconin carboxylic acid is easily available, this route is quite practical, contrary to the statement of Shamma[10]. An important route to the synthesis of the protoberberine skeleton is the Mannich cyclisation of a 1-benzyl-1, 2, 3, 4-tetrahydroisoquinoline. Mannich cyclisation with formaldehyde of 1-(3', 4-dimethoxybenzyl)-1. 2, 3, 4-tetrahydro-6,7-methylenedioxyisoquinoline(VII) leads to the formation of tetrahydro-ψ-berberine(VIII).

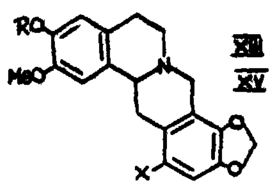


VII R=H ; X=H
IX R=H ; X=Br
X R=CHO ; X=Br

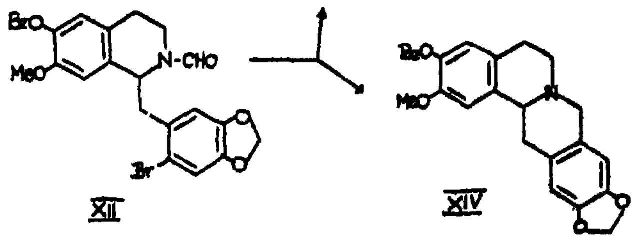
VIII R_1=H ; R_2=OMe X=H
XI R_1=OCH_3 ; R_2=H X=Cl

Since a vast majority of protoberberines are substituted in the 9,10-position, the method as such is limited in scope since it leads essentially to the 10, 11-oxygenated compounds. In order to force the cyclisation to take place at the 2'-position, bromine was used as the blocking group. Haworth and Perkin found however that the Mannich reaction did not at all proceed with the bromo compound IX[11]. However, the N-formyl derivative underwent cyclisation, giving only the ψ-berberine VIII. The authors remark that the tendency of cyclisation to the *para* position to the methoxy substituent was so great that the bromine was ejected.

A reinvestigation of the route employing bromine as a blocking group was considered desirable and it was first tested in the synthesis of dl-tetrahydrogröenlandicine[12]. Cyclisation of the bromoamide XII with $POCl_3$ yielded the protoberberine XIII



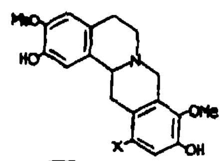
XIII : X=Cl & Br ; R=Bz
XV : X=H ; R=H



XII XIV

found to be a mixture of chloro and bromo compounds. This was indicated by the presence in the mass spectrum of peaks at m/e 405 and 403 (bromo compound) and 361 and 359 (chloro compound). Reductive cleavage of the halogen with 10% Pd/C in ethanol followed by debenzylation yielded dl-tetrahydrogröenlandicine(XV). The cyclisation product with the bromine ejected(XIV) was found to be the major compound (3 : 1).

By a similar procedure, with appropriate starting materials, the synthesis of dl-stepholidine(XVI) was achieved[13]. With the use of $POCl_3$, halogen exchange prevailed, the product of cyclisation being one in which the bromine had been replaced significantly by chlorine(XVII). It was however possible to reduce XVII to the desired tetrahydroprotoberberine XVI. The 10, 11-oxygenated compound,

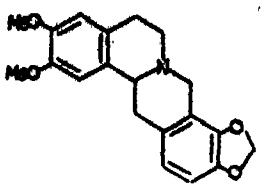


XVI X = H
XVII X = Cl and Br

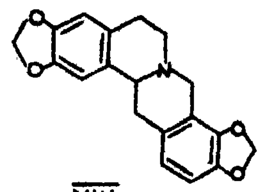
arising from displacement of bromine was also formed in considerable yield. In a reinvestigation of the work of Haworth and Perkin (*loc cit*) the bromoamide X was cyclised with $POCl_3$, followed by reduction with $NaBH_4$ to yield 12-chlorocanadine(XI). But attempts at replacement of chlorine by hydrogen failed. In order to avoid the halogen exchange, $POBr_3$ was used as a cyclising agent and after $NaBH_4$ reduction, 12-bromocanadine was obtained, which was hydrogenolysed to yield dl-canadine.

The major product in the $POBr_3$ cyclisation was however one in which the bromine had been ejected to give a 10, 11-oxygenated protoberberine. Using $POBr_3$ as a cyclising agent, it was possible to

accomplish syntheses of dl-sinactine(XVIII) and dl-stylopine(XIX)[14]. Perhaps, subtle factors such



XVIII

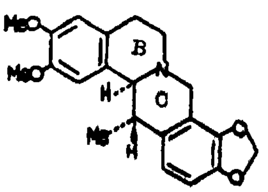


XIX

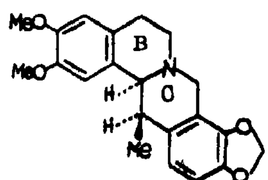
as the pattern of oxygen substitution or purity of the phosphorus oxychloride are at play in the cyclisation reaction, since Tani *et al*[15] succeeded in cyclising a bromoamide with $POCl_3$ without halogen exchange and obtained finally dl-cheilanthifoline.

Synthesis of Thalictrifoline :

The alkaloid thalictrifoline(XX) is unique in being the only naturally occurring 13-methyltetrahydroprotoberberine, with the B/C ring having a *cis*-quinolizidine conformation. Its C_{13} epimer, base II (Cavidine) (XXI) also occurs naturally and has been shown to have a B/C *trans*-junction.



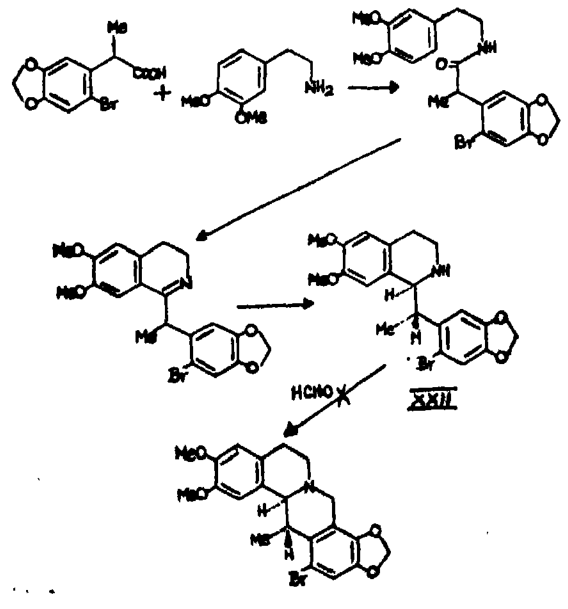
XX



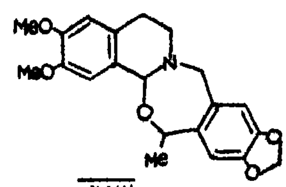
XXI

The synthesis outlined in Chart 2 is based on that of Shamma[16] for 13-methyltetrahydro-ψ-protoberberine with a modification involving the use of a

Chart—2



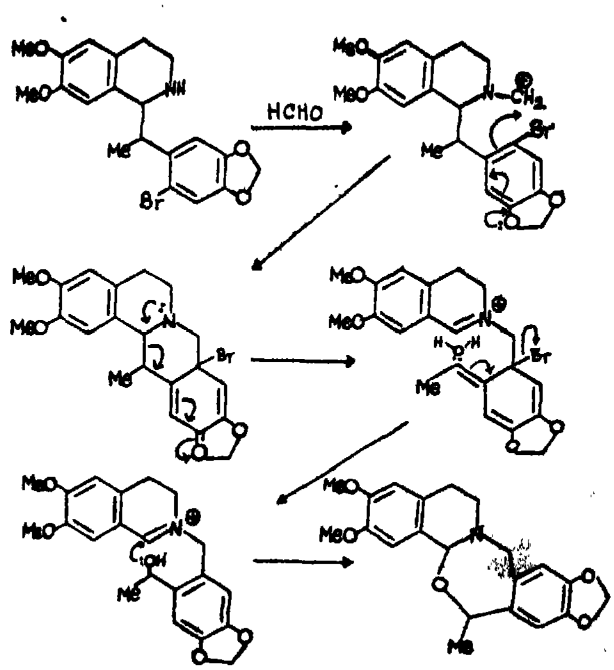
bromine as a blocking group to achieve a 9, 10-oxygenation pattern. The dihydroisoquinoline indicated in the scheme was easily prepared. Reduction yielded only one diastereoisomer, XXII which was shown to be the *erythro*-compound as indicated by the chemical shift of the C-methyl group (δ 1.23). The tetrahydroisoquinoline on being heated with formaldehyde and acid under a variety of conditions did not yield the expected tetrahydroprotoberberine, but a product, m.p. 210° to which structure XXIII has been assigned on the basis of extensive spectral data and degradation



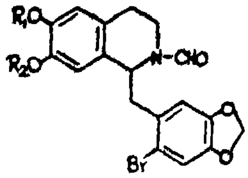
XXIII

studies[17]. The structure has been confirmed by an X-ray crystallographic study[18] which has also revealed the relative stereochemistry. The formation of structure XXIII has been rationalised in terms of the reaction mechanism depicted in Chart 3.

Chart-3



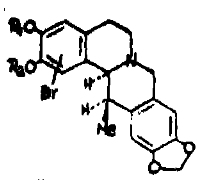
Not being succeeded in achieving a Mannich cyclisation, attention was turned to the N-formyl derivative(XXIV). This was submitted to the Bischler-Napieralsky reaction under a variety of conditions. It was found that with both $POCl_3$ and $POBr_3$, the bromine atom was ejected giving



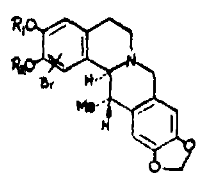
XXIV $R_1 = R_2 = Me$
XXVII $R_1 + R_2 = {>}CH_2$

a 10, 11-oxygenated product, which was reduced with $NaBH_4$ to a mixture of C_{13} methyl epimers. When an undistilled sample of $POBr_3$ was used a bromo compound was obtained in poor yield. The yield of the bromo compound was improved by using a mixture of PBr_3 and P_2O_5[19]. After reduction of the crude product with $NaBH_4$, four products were isolated, two of which were identical with the bromine-free C_{13}-methyl epimers, belonging to the pseudotetrahydroprotoberberine series (10, 11-oxygenated). The two bromine-containing compounds gave the same two epimers on reductive debromination. It was therefore clear that the cyclisation of the bromoamide(XXV) has only been accomplished at the site of the bromine atom after its expulsion, followed by nuclear bromination.

The structures of these two compounds were assigned as XXV and XXVI on the basis of NMR and mass spectral data[19]. The compound m.p. 146°



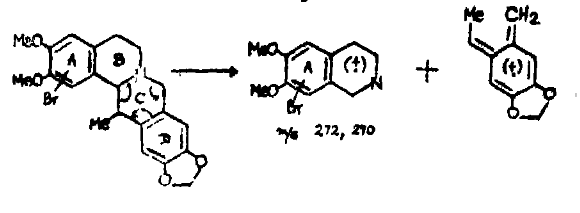
XXV $R_1 = R_2 = CH_3$
XXVIII $R_1 + R_2 = {>}CH_2$



XXVI $R_1 = R_2 = CH_3$
XXIX $R_1 + R_2 = {>}CH_2$

had an Rf ($CHCl_3$: MeOH : EtOAC 40 : 1 : 2.5) of 0.9, rate of methiodide formation 1.3×10^{-4} S^{-1} (31.5°), a methyl doublet in the NMR (J = 7Hz) at δ0.93 corresponding to the C_{13}-methyl group and a broad singlet and δ3.75 (C_8H). The other compound m.p. 160° had an Rf 0.5, rate of methiodide formation 99.6×10^{-4} S^{-1}, a methyl doublet at δ1.47 (J = 7Hz) and an AB quartet at δ3.71 (J = 16Hz) and δ4.16 (J = 16Hz) corresponding to the methylene at C_8. On the basis of this evidence, the former was assigned the *trans*-quinolizidine structure XXV and the latter the *cis*-quinolizidine structure XXVI. The mass spectra of both compounds showed typical fragmentation characteristic of tetrahydroprotoberberines as shown in Chart 4. This indicated that the bromine was in ring A. It was considered likely to be in position 4.

Chart-4



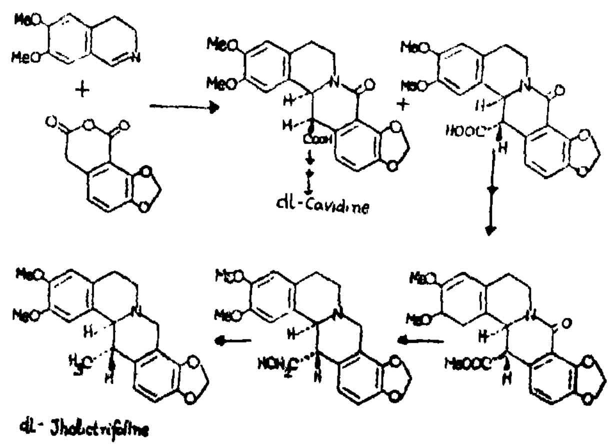
However, there was no easy way of proving this by chemical degradation. A pair of compounds similar to the two compounds discussed above were obtained from the amide XXVII. These were assigned the structures XXVIII and XXIX on the basis of NMR spectra and other physical data. X-ray crystallographic analysis of the two compounds were carried out by Prof. Rogers at the Imperial College, London[20].

X-ray analysis of the compound, m.p. 205-206°, assigned the *trans*-quinolizidine structure revealed that the bromine was in position 4. But there was evidence that some 4 per cent of the molecules carry bromine at C_9 as well as for minor amounts of a 4, 9-dibromo compound. The transfusion of the quinolizidine viz. XXVIII assigned[19] on the basis of physical data was fully confirmed.

X-ray analysis of the compound m.p. 179° confirmed the presence of a *cis*-quinolizidine system (XXIX) and the presence of bromine at position 4. These X-ray studies constitute the first example of such a study on a pair of epimeric 13-methyl tetrahydroprotoberberines and help to give credence to the conclusions on B/C-ring geometry based hitherto on NMR and other physical data.

The synthesis of dl-thalictrifoline and dl-cavidine was finally accomplished by the route shown in Chart 5[21]. The route is based on a procedure developed by Cushman *et al*[22].

Chart-5

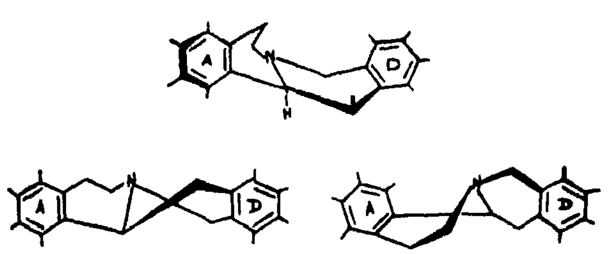


Stereochemical aspects of tetrahydroprotoberberines :

It has been well established that all tetrahydroprotoberberines with a negative rotation have a 14 R configuration[23]. However, this can be applied only to compounds unsubstituted at C_{13} and C_8 with confidence.

The tetrahydroprotoberberines are dibenzo-(a,g)-quinolizidines and due to the conformational mobility of the nitrogen atom, it is possible to write one *trans*-quinolizidine and two *cis*-quinolizidine conformations for any structure. It is assumed that the two rings (B and C) have a quasi-chair conformation. These are depicted in Chart 6. The actual

Chart - 6



conformation of a compound is decided by the nature of the substitution at position 1, 8 or 13. In compounds unsubstituted at these positions the *trans*-quinolizidine conformation will prevail, being thermodynamically, the most stable. Generally, such compounds display in the IR spectra prominent peaks in the 2700-2800 cm^{-1} region, named the Bohlmann bands. Kessar has pointed out that the Bohlmann bands can only detect the *trans*-fused conformation and cannot rule out the presence of substantial quantities of the *cis*-conformation[24].

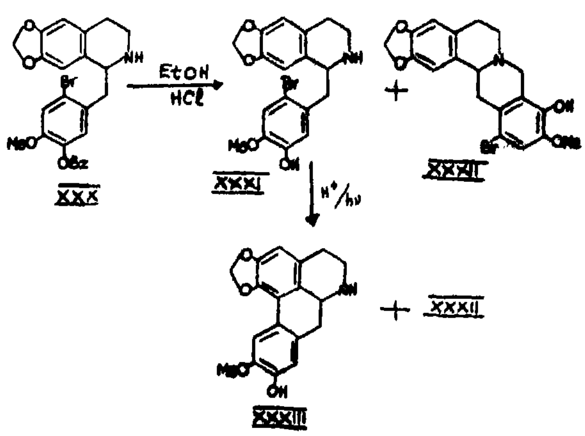
Takao and Iwasa[25] have made a detailed spectroscopic study of 22 tetrahydroprotoberberines and have derived some valuable conclusions. 13-methyltetrahydroprotoberberines, which have the C_{13} hydrogen and C_{14} hydrogen *cis* exist almost exclusively in the *trans*-quinolizidine form. Those in which these two hydrogen have a *trans*-relationship exist almost entirely in the *cis*-quinolizidine form. In the case of compounds which have an oxygen substituent at C_1, the *cis*-quinolizidine form predominates, but there is always some amount of the *trans*-quinolizidine, which decreases with the increasing bulk of the C_1-substituent.

NMR spectroscopy has been of great value in assigning conformation to 13-methyltetrahydroprotoberberines. The chemical shift of the C_{13} methyl group in compounds with *trans*-fused B/C rings (C_{13}H and C_{14}H *cis*) is between δ0.90-1.00, while it is at δ1.40-1.50 in the *cis*-fused B/C ring compounds (C_{13}H and C_{14}H *trans*). In the spectra of *trans*-fused 9, 10-dioxygenated-13-methyltetrahydroprotoberberines the C_8 protons appear as an AB quartet with a large difference[25], in chemical shift, while in the corresponding *cis*-quinolizidine, the shift difference is smaller. Recently Cushman *et al.*[23] pointed out that the C_8 proton in the B/C *cis*-fused 10, 11-dioxygenated tetrahydroprotoberberines, the protons at C_8 appeared as two doublets (J=16 Hz) at *Ca* δ3.7 and δ4.2, while a broad singlet corresponding to these protons showed up at *Ca* δ3.7 in the *trans*-fused compound.

Pai *et al.*[26] carried out a 90 MHz NMR study of several 9, 10- and 10, 11-dioxygenated tetrahydroprotoberberines. They concluded that the C_8 protons are observed as an AB quartet whether the B/C ring fusion was *cis* or *trans* irrespective of the oxygenation pattern. The centre of the AB quartet appears relatively downfield in all cases of *cis*-quinolizidines as compared to the *trans*-quinolizidines by about 0.15-0.20 ppm. In 10, 11-dioxygenated compounds, the signals of the C_8 protons are separated by 0.45-0.48 ppm in the *cis*- and 0.40-0.48 ppm in the *trans*-quinolizidines, while the corresponding values in 9, 10-oxygenated compounds are 0.13-0.18 and 0.55-0.72 ppm. The most consistent and dramatic difference between the *cis*- and *trans*-quinolizidines is seen in the chemical shift of the methyl group at C_{13}. These values range from δ1.43-1.48 for the *cis* and δ0.88-0.99 for the *trans*-series, irrespective of the oxygenation pattern.

An unintended route to tetrahydroprotoberberines :

Lastly, brief mention may be made of the formation of tetrahydroprotoberberines during the course of debenzylation of certain 1-benzyl-1, 2, 3, 4-tetrahydroisoquinolines[27]. Thus debenzylation of 1-(3-benzyloxy-6-bromo-4-methoxybenzyl)-6, 7-methylenedioxy-1,2,3,4-tetrahydroisoquinoline(XXX) gave the corresponding hydroxy compound (XXXI) as well as 12-bromo nandinine(XXXII) which could be debrominated to nandinine. Irradiation of the 2-bromo-

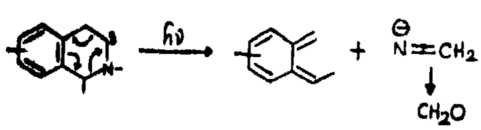


3-hydroxy-4-methoxybenzyl-6,7-methylenedioxy 1, 2, 3, 4-tetrahydroisoquinoline gave the aporphine (XXXIII) as also the compound XXXII. Although the yield of the tetrahydroprotoberberine is very low, its formation is intriguing. Detailed studies were carried out on both debenzylation and photolysis of a variety of 1, 2, 3, 4-tetrahydroisoquinolines[27] which depict the conditions needed for the formation of the tetrahydroprotoberberines. These are : (a) the nitrogen has to be secondary ; (b) the position adjacent to the benzylic carbon on the potential ring D has to be activated by a suitably positioned hydroxy group. Under photolytic conditions, tetrahydroprotoberberine formation will take place if these conditions are met. However for this to take place under debenzylation conditions, a methoxyl or methylenedioxy group has to be present in the structure.

The one-carbon unit furnishing the berberine bridge apparently arises from the methylenedioxy or methoxy group present, under debenzylation conditions. The formation of formaldehyde from the methylenedioxy function is easily understood but its formation from methyl halide or methanol released from methoxyl function needs a further oxidation stage and the mechanism is not obvious.

Photolysis of 1, 2, 3, 4-tetrahydroisoquinoline in aqueous acidic medium generated formaldehyde (Chart 7).

Chart-7



An explanation would be a retro-Diels-Alder reaction releasing C_3 of the isoquinoline as formaldehydeimine.

Although the first alkaloid berberine was isolated some 150 years ago, interest in this group of compounds has not abated. There is a large volume of interesting work both as regards synthesis as well as reactions of this class of alkaloids which are being constantly brought out.

In this lecture our attention has been confined to the work carried out at Presidency College, Madras largely under the guidance of Prof. B. R. Pai and Dr. K. Nagarajan. I am grateful to them for valuable help in the preparation of this lecture.

References

1. P. W. Jeffs, The Alkaloids ed. R. H. F. Manske, Academic Press, New York, 1967, p. 41-115., Vol. IX.
2. (a) M. Shamma, The Isoquinoline alkaloids, Academic Press, New York, 1972, p. 268-314.
   (b) M. Shamma and J. L. Moniot, Isoquinoline alkaloids Research, 1972-1977, Plenum Press, New York and London, p. 209-260.
3. S. F. Dyke in Rodd's Chemistry of Carbon Compounds, Elsevier, Vol. IV, Part H, p. 110-145.
4. B. R. Pai, K. Nagarajan, H. Suguna and S. Natarajan, *Heterocycles*, 1977, **6**, 1377.
5. T. R. Govindachari and S. Rajadurai, *J. Chem. Soc.*, London, 1957, 557.
6. W. H. Perkin Jr., J. N. Ray and R. Robinson, *J. Chem. Soc.*, London, 1925, **127**, 740.
7. M. Ohta, H. Tani and S. Morozumi, *Tet. Lett.*, 1963, 859.
8. T. R. Govindachari, S. Rajadurai, M. Subramaniam and N. Viswanathan, *J. Chem. Soc.*, London, 1957, 2943.
9. T. R. Govindachari, S. Rajadurai and C. V. Ramadoss, *Chem. Ber.*, 1959, **92**, 1654.
10. M. Shamma, The Isoquinoline alkaloids, Academic Press, New York, 1972, p. 278.
11. R. D. Haworth and W. H. Perkin Jr., *J. Chem. Soc.*, 1925, **127**, 1448.
12. H. Suguna and B. R. Pai, *Coll. Czech. Commun.*, 1976, **41**, 1219.
13. S. Rajeswari, H. Suguna and B. R. Pai, *Coll. Czech. Commun.*, 1977, **42**, 2207.
14. R. Rajaraman, B. R. Pai, M. S. Premila and H. Suguna, *Indian J. Chem.*, 1977, **15B**, 876.
15. O. Tani, S. Takao, H. Endo and E. Oda, *J. Pharm. Soc.*, Japan, 1973, **93**, 268.
16. M. Shamma, C. D. Jones and J. A. Weiss, *Tetrahedron*, 1969, **25**, 4347.
17. S. Natarajan, B. R. Pai, R. Rajaraman, H. Suguna, C. S. Swaminathan, K. Nagarajan and V. Sudarsanam, *J. Chem. Soc., Perkin Transaction I*, 1979, 283.
18. S. Natarajan, B. R. Pai, R. Rajaraman, C. S. Swaminathan, K. Nagarajan, V. Sudarsanam, D. Rogers and A. Quick, *Tet. Lett.*, 1975, 3573.
19. B. R. Pai, S. Natarajan, G. Manikumar, R. Rajaraman and H. Suguna, *J. Org. Chem.*, 1978, **43**, 1992.
20. Prof. D. Rogers, Private Communication—To be published.
21. Prof. B. R. Pai, Private Communication—To be published.
22. M. Cushman, J. Gentry and F. W. Dekow, *J. Org. Chem.* 1977, **42**, 1111.
23. T. Kametani and M. Ihara, *J. Chem. Soc.*, 1968, 1305.
24. S. V. Kessar, *Experientia*, 1962, **18**, 56.
25. N. Takao and K. Iwasa, *Chem. and Pharm. Bull.* (Japan), 1976, **24**, 3185.
26. B. R. Pai, K. Nagarajan, H. Suguna and S. Natarajan, *Heterocycles*, 1978, **9**, 1287.
27. T. R. Govindachari, K. Nagarajan, S. Rajeswari, H. Suguna and B. R. Pai, *Helv. Chim Acta*, 1977, **60**, 2138.

J. Indian Chem. Soc.,
Vol. LVII, April 1980, pp. 359-362

Studies on Mixed Ligand Complexes of Copper. Part III. Copper-Lactate-Aminocarboxylate Complexes

V. V. RAMANUJAM* and U. KRISHNAN

Department of Inorganic Chemistry, University of Madras, A. C. College Buildings, Guindy, Madras-600 025

Manuscript received 16 November 1979, accepted 20 December 1979

Formation and stability of mixed-ligand complexes of Cu^{2+} with lactic acid as primary ligand and some amino acids as secondary ligands were determined by pH-metry and by spectrophotometry at 30° and at $\mu = 0.25$ (KNO_3). $\Delta \log K$ and $\log X$ values indicate the favoured formation of these mixed-ligand complexes with heterodonor atoms when compared to mixed-ligand complexes with identical donor atoms. The factors affecting the formation and stability of the mixed-ligand complexes are discussed.

THE increasing number of studies on formation of mixed-ligand complexes reveals a realisation of their growing importance, particularly in their role in biological processes. The formation of such complexes is a general feature of systems where a metal is present with two or more ligands. An analysis of the formation constant data on these complexes shows that their formation is a favoured process over that of simple complexes. A survey of the literature shows that studies undertaken involve mostly complexes formed by amines and amino acids and to some extent, phenols and phenolic acids[1-4]. Study of complexes involving aliphatic hydroxy acids should provide interesting information since the hydroxo group is weak in its tendency to co-ordination[5,6]. Weak bonding by OH groups of glycollic, lactic and some hydroxy amino acids present in biological systems is believed to aid enzyme catalysis. Study of mixed-ligand formation with lactic acid as one of the ligands was undertaken as part of a systematic study involving hydroxy acids.

The present work reports the study of the formation of ternary complexes of copper with lactic acid and aminocarboxylic acids by spectrophotometry. The results obtained have been checked by *p*H metric studies.

Experimental

Reagents : All reagents used were from standard manufacturers and of high purity. All the solutions are made in double distilled water and estimated by standard procedures.

Measurements :

(i) *pH-metry :* The titrations were carried out under nitrogen atmosphere in th solutions at constant ionic strength, $\mu = 0.25$ (KNO_3) in a thermostatted bath at $30 \pm 0.1°$. A digital *p*H meter (ECIL, *p*H 822A, accuracy $\pm$ 0.01 *p*H unit) was used to measure the *p*H. The instrument was calibrated before each titration with 0.05*M* potassium hydrogen phthalate, *p*H 4.01 at 30°.

Absorbance Measurements : The absorbance measurements were made with a Carl Zeiss single beam spectrophotometer, model VSU-2P, with matched 1 cm glass cells. Here also the measurements were made at $\mu = 0.25$ (KNO_3) and the cells were thermostatted at $30.0 \pm 0.1°$.

Ionisation Constants of the Ligands : The ionisation constant of lactic acid was determined under our laboratory conditions by the method of Albert and Sergeant[7]. The ionisation constants for other ligands were taken from our earlier work[8].

Formation Constant of the Binary Complexes : The formation constants of all amino acids were taken from our earlier work[8]. The values for lactic acid were taken from literature[9].

Formation Constants of the Mixed-ligand Complexes (pH-metry) :

The formation of the mixed-ligand complexes were studied under the same conditions for binary complexes, except that the solutions contained both ligands. In solutions containing equal amounts of lactic acid and amino acid, hydrolysis starts even at low *p*Hs. Calculations yielded good results when lactic acid and amino acid are present in the ratio of 4 : 1.

Spectrophotometry : Absorbance measurements were made with solutions containing a fixed amount of Copper(II) and varying amounts of the two ligands – always keeping the total concentration of the two ligands many times greater than that of the metal. Before and after the absorbance measurements the *p*H of the solution was measured.

Calculation :

1. Spectrophotometry : The method proposed by Newman and Hume[12] is applied to the calculation of the formation constant of the mixed-ligand complex. This method is a highly generalised method, applicable to nearly all the systems, but very much complicated. The treatment gets much simplified when only one mixed-ligand complex is formed as in the case of a metal like copper with two bidentate ligands.

When the concentrations of the two ligands is maintained very high compared to Cu(II), it can be safely assumed that the higher complex, binary or ternary would be present at all times. Then

$$\bar{A} = \epsilon_{CuA_2}[CuA_2] + \epsilon_{CuAB}[CuAB] + \epsilon_{CuB_2}[CuB_2] \quad \ldots (1)$$

For the equilibrium

$$CuB_2 + A \rightleftharpoons CuBA + B \quad \ldots (2)$$

$$K_{form} = \frac{[CuBA][B]}{[CuB_2][A]} \quad \ldots (3)$$

and for the equilibrium

$$CuBA + A \rightleftharpoons CuA_2 + B \quad \ldots (4)$$

$$K_{repl} = \frac{[CuA_2][B]}{[CuBA][A]} \quad \ldots (5)$$

with high concentration of only one ligand, e.g. A, CuA_2 would be present and the ϵ_{CuA_2} can be calculated.

$$Ao = \epsilon_{CuA_2}[Cu(II)] \quad \ldots (6)$$

When A>B then only CuA_2 and CuAB will be present under favourable *p*H conditions. Then,

$$\bar{A} = K_{repl}\left\{(A_o - \bar{A})\frac{A}{B}\right\} + \epsilon_{CuAB}[Cu(II)] \quad \ldots (7)$$

A plot of $\bar{A}$ vs $(A_o - \bar{A})\frac{A}{B}$ yields a straight line with K_{repl} as slope and from the intercept ϵ_{CuAB} can be calculated.

When A/B ratio is appreciable all the 3 species, CuA_2, CuAB and CuB_2 will be present and if a wavelength is so chosen that only CuA_2 and CuAB species absorb, then,

$$[(K_{repl}(A_o - \bar{A})A/B) - \bar{A}] = 1/K_{form}\{\bar{A} \times B/A\} - \epsilon_{CuAB}[Cu(II)] \quad \ldots (8)$$

Here a plot of the terms in the left-hand side vs the brace-enclosed terms yields a straight line with $1/K_{form}$ as slope and from the intercept ϵ_{CuAB} can be calculated. This permits a check on the value of ϵ_{CuAB}.

2. pH-metry : The following species were taken into account in the computation of the formation constant of the mixed-ligand complex HA, A, H_2B, HB, B, CuA, CuA_2, CuB, CuB_2, CuAB and Cu. Here HA and H_2B represent lactic acid and protonated amino acid respectively. Charges are not included for convenience. The method of calculation used is that of Nasanen and Koskinen[10,11] with slight modification.

Results and Discussion

The extent to which a mixed-ligand complex is favoured in formation is better expressed by terms such as Δlog K and log X than by log β_{CuAB}. log X can be obtained by considering a "disproportionation" reaction shown below,

$$CuA_2 + CuB_2 \rightleftharpoons 2CuAB \quad \ldots (9)$$

$$X = \frac{[CuAB]^2}{[CuA_2][CuB_2]} \quad \ldots (10)$$

$$\log X = 2\log \beta_{CuAB} - (\log \beta_{CuA_2} + \log \beta_{CuB_2}) \ldots (11)$$

The value of log X calculated on statistical basis only is 0.6[13]. Here an experimentally determined value of log X=0.6 or more clearly indicates the favoured formation of the mixed-ligand complex. Δ log K is derived from 1 : 1 binary complexes while log X is derived from 1 : 2 binary complexes.

$$Cu + B \rightleftharpoons CuB\,;\ K_{CuB} = \frac{[CuB]}{[Cu][B]} \quad \ldots (12)$$

$$CuA + B \rightleftharpoons CuAB\,;\ K_{CuAB} = \frac{[CuAB]}{[CuA][B]} \quad \ldots (13)$$

$$\Delta \log K = \log K_{CuAB} - \log K_{CuB} \quad \ldots (14)$$

From statistical considerations, the most appropriate value for Δ log K has been proposed to be -0.9[14] for a distorted octahedral complex of Cu(II) with bidentate ligands. Hence an experimentally determined value of Δ log K= -0.9 or more indicates favoured formation of the mixed-ligand complex.

In the *p*H-metric method the concentration of the ligand used is comparable to that of the metal ion. While in the spectrophotometric method it is kept very manyfold greater since no free metal ion should be present. Hence it is appropriate to calculate Δ log K from the results obtained from *p*H metric studies and log X from the spectrophotometric studies.

log β_{CuAB} and Δlog K values for the copper-lactate-aminocarboxylate complexes are given in Table 1. Titrations with varying concentrations of

the two ligands show no indication of the formation of complex species other than [Cu lact am].*

TABLE 1—log $\beta_{[Cu\ lact\ L]}$ AND Δlog K VALUES FOR THE MIXED-LIGAND COMPLEXES AT 30±0.1° AND AT μ=0.25 (KNO_3) OBTAINED BY pH METRIC METHOD

Sl. No.	L	log $\beta_{[Cu\ lact\ L]}$	Δlog K
1.	glycinate	10.91	+0.16
2.	α-alaninate	10.65	−0.04
3.	serinate	10.02	−0.03
4.	β-alaninate	9.97	+0.38

For all the systems the Δlog K value is much higher than that predicted on statistical grounds. This shows the highly favoured formation of these mixed complexes. This is further confirmed by the log X values obtained from the spectrophotometric studies.

At 900 nm, the molar absorptivity of $Cu(lact)_2$ is very high compared to that of the $Cu(gly)_2$. When the ratio of lact/gly is maintained very high and at pH>5.0 only $Cu(lact)_2$ and [Cu lact gly] are the species present, then eq. (7) is applicable. From a plot using this equation the value of K_{repl} obtained is 1.527×10^{-7} and $\epsilon_{[Cu\ lact\ gly]}$ is 21.8. If the ratio of lact/gly is maintained at a moderate level and the pH between 5 and 6, all the three species, $Cu(lact)_2$ and [Cu lact gly] and $Cu(gly)_2$ are present. But at 900 nm $Cu(lact)_2$ and [Cu lact gly] absorb appreciably and then eq. (8) is applicable. Using this equation the value of K_{form} obtained is 3.00×10^{-5} and $\epsilon_{[Cu\ lact\ gly]}$ is 21.5. In both cases the value of $\epsilon_{[Cu\ lact\ gly]}$ obtained is very nearly the same. This confirms the validity of the assumptions made. The overall formation constant of the mixed-ligand complex is calculated from both K_{repl} and K_{form}. The average of the value of log β_{CuAB} obtained and log X values calculated are given in Table 2. The log β_{CuAB} values obtained by spectrophotometric method agree well with those obtained by pH-metry.

TABLE 2—log $\beta_{[Cu\ lact\ L]}$ AND log X VALUES FOR THE MIXED-LIGAND COMPLEXES AT 30±0.1° AND AT μ=0.25 (KNO_3) OBTAINED BY SPECTROPHOTOMETRIC METHOD

Sl. No.	L	log $\beta_{[Cu\ lact\ L]}$	log X
1.	glycinate	10.74	2.33
2.	α-alaninate	10.22	1.56
3.	serinate	9.76	1.53
4.	β-alaninate	9.69	2.71

Four factors appear to be significant in determining the relative stabilities of the mixed-ligand complexes. They are, nature of the donor atoms, ring sizes, neutralisation of charge and steric effect.

* *abbreviations* : ala=α-alaninate, bala=β-alaninate, am=aminocarboxylate, bipy=2,2′-bipyridyl, en=ethylenediamine, gly=glycinate, glyK=glycollate, lact=lactate, mal=malonate, ox=oxalate, pn=1,3-propylenediamine, sal=salicylate and ser=serinate.

In [Cu lact am] complexes copper is co-ordinated to three oxygen atoms and one N atom. The Δlog K and log X values are higher than for those containing only nitrogen or only oxygen as the donor atoms as can be seen from Table 3. The indication is that copper prefers mixed donors for complexation rather than homo donors.

TABLE 3—Δlog K AND/OR log X VALUES OF SOME MIXED-LIGAND COMPLEXES OF COPPER(II)

Sl. No.	Mixed-ligand Complex	Δlog K	log X	Ref.
1.	[Cu ox mal]	—	0.92	15
2.	[Cu lact gly]	+0.16	2.33	This work
3.	[Cu lact ala]	−0.04	1.56	This work
4.	[Cu lact ser]	−0.03	1.53	This work
5.	[Cu lact bala]	+0.38	2.71	This work
6.	[Cu glyK gly]	−0.48	—	5
7.	[Cu sal ala]	—	2.08	16
8.	[Cu sal ser]	—	1.76	16
9.	[Cu bipy glyK]	−0.10	—	6
10.	[Cu ox en]	—	0.94	2
11.	[Cu ox pn]	—	3.14	2
12.	[Cu bipy en]	—	1.10	2

Δlog K and log X values for [Cu lact bala] are greater than those for the copper-lactate-α-aminocarboxylate systems. This indicates that copper mixed-ligand complexes having a five- and a six-membered ring in the same complex is preferred over those containing two five-membered rings. Examples given in Table 3, confirm this.

The 1 : 1 binary complexes of copper-lactate and copper-aminocarboxylate carry a +1 charge. The mixed-ligand complex is neutral. The formation of a neutral species appears to be a strong driving force for the favoured formation of the mixed-ligand complex. This may be one of the reasons for the enhanced value of Δlog K.

Eventhough the co-ordination tendency of the un-ionized hydroxyl group in lactic acid is weak, it is sufficient enough for the acid to function as a bidentate ligand. This is evident from the binary formation constants. In mixed-ligand complexes also, hydroxyl group participation in co-ordination is known[5,6]. Because of the weak co-ordination of the hydroxyl group in $Cu(lact)_2$ it prefers a stronger chelating ligand like glycine. Thus glycine preferentially replaces one lactate group to form [Cu lact gly]. The low pH and the low concentration of the glycinate ion do not favour much the formation of the $Cu(gly)_2$. This explains why the mixed-ligand complex formation is favoured and the observed log X value is higher.

In the case of the mixed-ligand complexes formed by α-amino acids, the Δlog K and log X values are the greatest for glycinate, α-alaninate comes next and serinate last. This trend may be attributed to steric factors.

The distribution of various species present in a particular system as a % of the total copper concentration and their variation with the pH of the solution gives a good idea of the favoured formation of mixed-ligand complexes as also pH effects. As a representative system [Cu lact gly] is presented in Fig. 1. Here the concentration of [Cu lact gly]

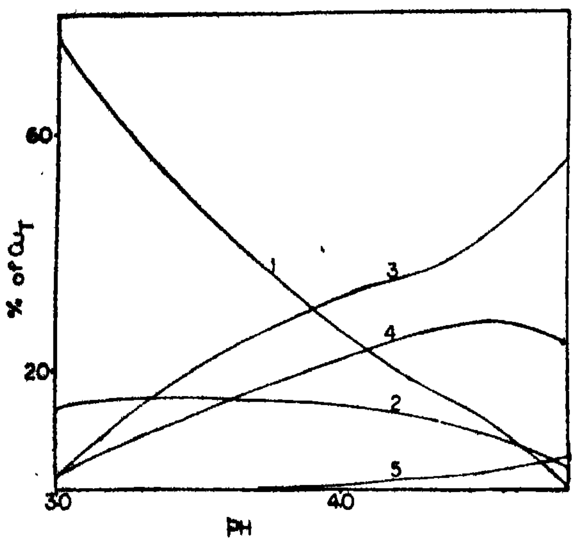


Fig. 1. The distribution of various species as a function of pH.
Curve : 1. Cu^{2+}, 2. [Cu lact], 3. [Cu lact gly], 4. [Cu gly], 5. $[Cu(gly)_2]$.

increases with pH. At 4.80 pH it reaches 55% of total copper. At low pH [Cu lact] complex is the major species present. As pH increases the concentration of $Cu(gly)_2$ species start rising. This is expected from the ionisation constants of the two ligands.

References

1. D. D. Perrin, I. G. Sayce and V. S. Sharma, *J. Chem. Soc.*, *A*, 1967, 1755.
2. H. Sigel, R. Caraco and B. Prijs, *Inorg. Chem.*, 1974, **13**, 462.
3. R. Griesser and H. Sigel, *Inorg. Chem.*, 1970, **9**, 1238.
4. G. A. L'Heureux and A. E. Martell, *J. Inorg. Nuclear Chem.*, 1966, **28**, 481.
5. R. P. Martin and R. A. Paris, *Bull. Soc. Chim. France*, 1963, 1600.
6. R. Griesser, B. Prijs and H. Sigel, *Inorg. Nuclear Chem. Lett.*, 1968, **4**, 443.
7. Adrien Albert and E. P. Serjeant, "The Determination of Ionisation Constants", Chapman and Hall Ltd., London, Second Edition, 1970.
8. V. V. Ramanujam and U. Krishnan, Communicated to *J. Inorg. Nuclear Chem.*
9. H. Thun, W. Guns and F. Verbeck, *Analyt. Chim. Acta*, 1967, **37**, 332.
10. R. Nasanen, P. Merilainen and S. Lukkari, *Acta. Chem. Scand.*, 1962, **16**, 2384.
11. R. Nasanen and M. Koskinen, *Suomen Kemistilehti*, 1967, **B40**, 23.
12. L. Newman and D. N. Hume, *J. Amer. Chem. Soc.*, 1957, **79**, 4571.
13. V. S. Sharma and J. Schubert, *J. Chem. Edn.*, 1969, **46**, 506.
14. H. Sigel, *Angew. Chem. Internat. Edit.*, 1975, **14**, 394.
15. I. J. Nigam, S. P. Saxena and C. M. Gupta, *Aust. J. Chem.*, 1975, **28**, 1617.
16. P. K. Migal and A. P. Gerbeleu, *Zhur. Neorg. Khim.*, 1967, **12**, 2695.

J. Indian Chem. Soc.,
Vol. LVII, April 1980, pp. 363-364

Mixed Chelate Complexes of Copper(II)

K. M. PUROHIT and D. V. RAMANA RAO

Department of Chemistry, Regional Engineering College, Rourkela-769 008

Manuscript received 9 November 1979, accepted 20 December 1979

Some mixed chelate complexes of Copper(II) of the type [Cu(dtc)(ox)] and [(Cu (β. dik) (ox)] where dtc = dithiocarbamate, β. dik = β. diketone and ox = oxine have been synthesised and characterised by elemental analyses, molar conductance, room temperature, magnetic moment, infrared and electronic spectral data. The complexes are paramagnetic and non-electrolytic in nature, having presumably square planar geometries.

DIVALENT copper forms several four-coordinated planar complexes both with mono- and bidentate ligands. Dithiocarbamates, β-diketones and oxine are uninegative bidentate ligands having –SS–, –OO– and –ON– donor sites. Further it was reported[1] that the antifungal action of dithiocarbamates is enhanced in the presence of cupric ion. Oxine is also known[2,3] to possess both antifungal and antibacterial properties. Hence it was thought worthwhile to study whether mixed chelate complexes of Copper(II) can be prepared containing these bidentates.

Experimental

Bis diethyl (Et_2 dtc), morpholyl (Morph. dtc) and piperidyl (Pip. dtc) dithiocarbamates of Copper(II) were prepared by known method[4]. *Bis* acetylacetonato (acac), benzoylacetonato (bzac) and dibenzoylmethenato (bzbz) Copper(II) were also prepared as per published method[5].

Reaction of bis dithiocarbamato Copper(II) with Oxine :

Bis dithiocarbamato Copper(II) compounds were reacted separately with oxine in 1 : 1 molar ratio in chloroform medium. The resulting solution was refluxed for one hour. The separated complexes were suction filtered, washed with ether and dried *in vacuo*.

Reaction of bis β-diketonato Copper(II) with Oxine :—

To a methanolic solution of $Cu(acac)_2$ an ethanolic solution of oxine was added in 1 : 1 molar ratio. The resulting solution was refluxed for one hour and the separated complex was suction filtered, washed with methanol followed by ether and dried *in vacuo*.

In case of $Cu(bzac)_2$ and $Cu(bzbz)_2$, the reaction with oxine in 1 : 1 molar ratio was carried out in chloroform medium. The resulting solution was refluxed for one hour for separating out the complex which was suction filtered, washed with ether and dried *in vacuo*.

Copper and Sulphur estimated by Standard Methods :

Infrared spectra in the range 5000-650 cm^{-1} were recorded on Nujol mulls using Unicam SP 200 double beam spectrophotometer. The magnetic susceptibilities were determined at room temperature on solid specimens using Gouy method. Diamagnetic corrections were made using Pascal's constants. The molar conductance was measured in $10^{-3}M$ acetone solution using Toshniwal conductivity bridge, type CLOIO2 and a dip type cell.

Results and Discussion

The analytical, molar conductance and magnetic susceptibility data are recorded in Table 1. Infrared and electronic spectral data are recorded in Table 2.

All the compounds are non-electrolytes as indicated by the low molar conductance values, (See Table 1). Magnetic susceptibility measurements indicate that all the complexes are paramagnetic with one unpaired electron as expected for a $3d^9$ cupric ion. The values of the magnetic moments for square

TABLE 1—ANALYSES, MELTING POINTS, MOLAR CONDUCTANCE AND MAGNETIC MOMENT VALUES OF MIXED CHELATE COMPLEXES OF Cu(II)

Complexes	Colour	M.P. °C	%Cu Found/cal	%S Found/cal	Λ_m (mhos)	μ_{eff} (B.M.)
[Cu(Et_2dtc)(OX)]	Shining black	200	17.52/17.87	18.33/18.00	0.68	1.80
[Cu(Morph.dtc) OX)]	Brown	280	16.90/17.19	17.50/17.31	0.65	1.85
[Cu(Pip.dtc)(OX)]	Green	224	17.45/17.28	17.10/17.41	0.60	1.88
[Cu(acac)(OX)]	Green	225	20.51/20.72	—	0.98	1.86
[Cu(bzac)(OX)]	Green	220	16.95/17.24	—	0.89	1.83
[Cu(bzbz)(OX)]	Green	220	14.50/14.75	—	0.82	1.85

TABLE 2—INFRARED AND ELECTRONIC SPECTRAL DATA (IN cm^{-1}) OF MIXED CHELATE COMPLEXES OF Cu(II)

Complex	dithiocarbamate			Oxine	λ_{max}
	$\nu C-N$	$\nu_{as}C-S$	$\nu_s C-S$	$\nu C-O$	
[Cu(Et$_2$dtc)(OX)]	1510	990	710	1120	16393
[Cu(Morph.dtc)(OX)]	1490	1000	710	1100	16129
[Cu(Pip.dtc)(OX)]	1510	1000	720	1100	16393
	β-diketone			Oxine	λ_{max}
	$\nu C=O$	$\nu C=C$		$\nu C-O$	
[Cu(acac)(OX)]	1600	1560		1120	16500
[Cu(baac)(OX)]	1600	1580		1100	16500
[Cu(babs)(OX)]	1600	1560		1100	16000

planar Copper(II) complexes lie in the range 1.83-1.86 B.M.[6,7], whereas for tetrahedral configuration, the moments will be larger than 2.0 B.M. In the present case, μ_{eff} values of the complexes suggest square planar structure.

Infrared Spectra :

The relevant infrared absorption bands due to the coordinated chelates in the complexes with their possible assignments are given in Table 2. Many bands due to oxine are found to be overlapping with the bands of dithiocarbamates. However, the most characteristic bands which could be definitely assigned were given in the table. The $\nu C-N$ and $\nu C-S$ bands due to dithiocarbamates indicate clearly that they are coordinated to the metal ion through both the sulphur atoms[9]. In the β-diketonato complexes the bands due to $\nu C=O$ and $\nu C=C$ were observed in the region 1600 cm^{-1} and 1570 cm^{-1} respectively as expected, indicating the presence of coordinated carbonyl group of β-diketone[10]. In addition to the bands cited above, a strong band round about 1100 cm^{-1} was also observed. Charles *et al*[11] reported that in several oxine complexes of metals, $\nu C-O$ was observed at 1120 cm^{-1} region, the position of the band slightly varying with the metal. In the present investigation, the invariable presence of strong band at 1100 cm^{-1} definitely indicates the presence of oxine group in the complex.

Electronic Spectra :

Though three transitions $2B_{1g}\rightarrow 2A_{1g}$, $2B_{1g}\rightarrow 2B_{2g}$ and $2B_{1g}\rightarrow 2E_g$ are expected for Copper(II) complexes, they are very close in energy and often give rise to one broad band envelop. Sacconi[6] and Meek and Ehrhardt[12] have observed that square planar complexes have a complex broad band at relatively higher frequencies (16,000 cm^{-1}). The regular tetrahedral complexes of Copper(II) show no d – d absorption bands in the region 10,000-20,000 cm^{-1} [13]. The spectra of all the mixed chelate complexes now studied display a broad band around 16,000 cm^{-1} which may be assigned to a combination of the two transitions $2B_{1g}\rightarrow 2A_{1g}$ and $2B_{1g}\rightarrow 2E_g$ in D4h symmetry[14]. The position of this absorption band (16,000 cm^{-1}) is in agreement with those generally observed for planar Copper(II) complexes[15-18].

Thus, the compounds reported now are definitely four-coordinated mixed chelate complexes of Copper(II) with presumably square planar geometry.

References

1. A. SHULMAN and F. P. DWYER in "*Chelating Agents and Metal Chelates*" (Ed.) F. P. DWYER and D. P. MELLOR, Academic Press, New York, 1964, p. 393.
2. A. ALBERT, in "*The Strategy of Chemotherapy*" *Symposium SOC. Gen. Microbiol*, 1958, **8**, 112.
3. A. ALBERT, "*Selective Toxicity*", Methuen, London, 1960.
4. R. N. DASH and D. V. RAMANA RAO, *J. Indian Chem. Soc.*, 1975, **52**, 1009.
5. T. SHIGEMATSU, M. TABUSHI, M. MATSUI and M. MUNAKATA, *Bull. Chem. Soc.* Japan, 1968, **41**, 2656.
6. L. SACCONI and M. CIAPOLINI, *J. Chem. Soc.*, 1964, 278.
7. S. F. A. KETTLE, in "*Coordination Compounds.*" Nelson, London, 1975, p. 185.
8. B. N. FIGGIS, *Nature*, 1958, **182**, 1568.
9. R. M. GOLDING, C. M. HARRIS, K. J. JESSOP and WC. TENNANT, *Aust. J. Chem.*, 1972, **25**, 2567.
10. K. NAKAMOTO "*Infrared Spectra of Inorganic and Coordination Compounds*". John Wiley and Sons, New York, 1969.
11. R. C. CHARLES, H. FREISER, R. FRIEDEL, L. E. HILLARD and W. D. JOHNSTON, *Spectro. Chim. Acta*, 1956, **8**, 1.
12. D. W. MEEK and S. A. EHRHARDT, *Inorg. Chem.*, 1965, **4**, 584.
13. A. B. P. LEVER, "*Inorganic Electronic Spectroscopy*", Elsevier, Amsterdam, 1968, p. 359.
14. B. N. FIGGIS, "*Introduction to Ligand Fields*", Interscience, New York, 1967, p. 316.
15. L. E. ORGEL, *J. Chem. Phys.*, 1956, **23**, 6.
16. N. M. KARAYANNIS, C.M. MUKULSKI, L. L. PYTLEWSKI and M. M. LABES, *J. Inorg. Nuclear Chem.*, 1972, **34**, 3139.
17. W. BYERS, A. B. P. LEVER and R. V. PARISH, *Inorg. Chem.*, 1968, **7**, 1835.
18. N. M. KARAYANNIS, L. L. PYTLEWSKI and M.M. LABES, *Inorg. Chim. Acta*, 1969, **3**, 415.

J. Indian Chem. Soc.,
Vol. LVII, April 1980, pp. 365-367

Coordination Chain Polymers of Schiff Base Derived from Ortho-Aminobenzoic Acid and Terephthalaldehyde

BHAGWAT SINGH, VISHWANATH BANERJIE, B. V. AGARWALA and ARUN K. DEY*

Chemical Laboratories, University of Allahabad, Allahabad-211 002

Manuscript received 24 September 1979, accepted 30 December 1979

The Schiff base synthesised by condensing *o*-aminobenzoic acid and terephthalaldehyde in ethanolic medium, forms complexes $[ML.2H_2O]_n$ with Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II). These were obtained by refluxing the metal : ligand : : 1 : 1 in dimethylformamide. The polymeric octahedral structures of the insoluble complexes have been arrived at on the basis of elemental, ir and rs studies, magnetic measurements and thermal analysis.

THIS paper is in continuation of earlier publications[1,2] from these laboratories, on the syntheses of new coordination polymers. The present communication describes the synthesis of Schiff base by the condensation of *o*-aminobenzoic acid and terephthalaldehyde, and the syntheses of metal chelates with Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II). The structures of the polymeric metal-chelates were established from data on elemental analyses, *infra-red spectra, electronic spectra, magnetic* susceptibility and thermogravimetric measurements.

Experimental

Chemicals employed were of analytical reagent grade and used without further purification.

Ethanolic solutions of *o*-aminobenzoic acid (13.7 gms) and terephthalaldehyde (6.7 gms) were mixed and a yellow crystalline solid Schiff base was obtained immediately. The mixture was heated on water bath for 1 hr and the solid filtered, washed successively with water and ethanol, and dried. It is insoluble in common organic solvents like benzene, chloroform, acetone, but highly soluble in dimethylformamide. Calculated for $C_{22}H_{16}N_2O_4$: C, 70.96 ; H, 4.30 ; N, 7.52. Found : C, 70.80 ; H, 4.54 ; N, 7.28%.

The metal acetate in dimethylformamide (DMF) was slowly added to a DMF solution of the ligand. In all the cases precipitation occurred almost immediately upon mixing the two reactants, but the mixtures were refluxed for 4 hr at 120° to ensure complete precipitation and allowed to cool overnight at room temperature. The metal chelates were filtered, washed with DMF and dried. The polymeric chelates are insoluble in all common organic solvents like acetone, ethanol, chloroform, methanol, benzene, DMF and DMSO.

* To whom all correspondence should be addressed.

Results of C, H, N and M analyses are given in Table 1.

TABLE 1—ANALYTICAL DATA

Complex	Colour	Decomposition Temperature (°C)	Elemental analysis Found (Calc) % C	H	N	M
$(MnL.2H_2O)_n$	Yellowish brown	360	58.28 (58.62)	2.76 (3.10)	5.89 (6.10)	12.83 (12.19)
$(CoL.2H_2O)_n$	Greenish brown	400	56.51 (56.78)	3.66 (3.87)	5.73 (6.02)	12.08 (12.66)
$(NiL.2H_2O)_n$	Yellow	400	56.54 (56.81)	3.47 (3.87)	5.58 (6.02)	12.25 (12.63)
$(CuL.2H_2O)_n$	Green	300	56.00 (56.28)	3.26 (3.83)	5.25 (5.96)	13.38 (13.52)
$(ZnL.2H_2O)_n$	Bright yellow	420	56.63 (56.00)	3.69 (3.81)	5.27 (5.93)	14.18 (13.87)
$(CdL.2H_2O)_n$	Yellow	460	50.62 (50.92)	3.28 (3.47)	6.04 (5.40)	21.47 (21.68)

Infra-red spectra were recorded in KBr pellets in the range of 4000-400 cm^{-1} using a Perkin-Elmer-577 Grating Infra-red Spectrophotometer.

Electronic reflectance spectra were obtained on a manual reading spectrophotometer using MgO.

Magnetic susceptibility measurements were made at room temperature by the Faraday method.

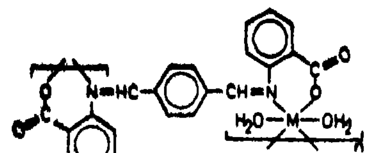
Thermal decomposition was studied by heating the samples at the rate of 10°/min and heated up to 800°.

Results and Discussion

The *ir* spectrum of the Schiff base shows a weak band at 2640-2500 cm^{-1}, which is assigned to hydrogen bonded O–H stretching of carboxylic groups[3]. This band vanishes in the spectra of

complexes, indicating the involvement of carboxylic OH in complexation. The strong band at 1680 and 1350 cm^{-1} due to C=O and C−OH stretchings in the ligand[4], disappear on complexation, and are replaced by two equivalent C−O bonds intermediate in force constant between C=O and C−OH[5]. Asymmetric and symmetric COO stretchings appear at 1540 and 1385, 1550 and 1380, 1555 and 1390, 1545 and 1400, 1540 and 1390, and 1540 and 1380 cm^{-1} in Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes respectively. Nakamoto has pointed out that the separation may be taken as covalence in M−O bond. The O−H in-plane and out-of-plane deformations at 1285 and 950 cm^{-1} in the Schiff base vanishes in the complexes supporting coordination through COOH. Ligand shows C=N stretching at 1625 cm^{-1} which shifts to 1620-1615 cm^{-1} on complexes indicating the involvement of azomethine N in coordination[7]. The bands at 3500-3400, 1695-1690 and 840-820 cm^{-1} are attributed to O−H stretching, HOH bonding and M−OH$_2$ stretching[6].

The complexes of bivalent metals with the Schiff base are extremely insoluble. The elemental analyses are in reasonably good agreement with a ligand to metal ratio 1 : 1, which is approached as polymerization is achieved. The following structure may be suggested.



This ligand : metal ratio does not permit a monomeric complex to exist since the four coordinating groups of one ligand molecule cannot attach to a single metal ion and attachment of the two groups at one end of the molecule would not satisfy the charge requirement of the metal(II) ions.

The positions of *d-d* bands and their assignments[8] are given in Table 2. A magnetic moment value of 5.52 BM for Mn(II) is less than that generally observed for octahedral complexes. This may be explained by the assumption of antiferromagnetic interaction between the Mn(II) ions in solid state[9]. Co(II) exhibits a magnetic moment of 5.20 BM as expected for octahedral complexes[10]. In the drs, the bands at 475 and 820 nm have been assigned for octahedral Co(II) but the transition $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ is not seen due to limited spectral range. Ni(II) complex is octahedral as evidenced by drs and magnetic moment of 3.19 BM[10]. Cu(II) shows a broad band at 500 nm, assigned to $^2E_g \rightarrow {}^2T_{2g}$ for distorted octahedral complex ; the broadening of band may be due to Jahn-Teller effect[11].

TABLE 2—ELECTRONIC SPECTRA AND MAGNETIC MOMENT

Complex	μ_{eff}(BM)	Band Position (nm)	Assignment
Mn(II)	5.52	580	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$
		500	$^6A_{1g} \rightarrow {}^4T_{2g}(G)$
		455	$^6A_{1g} \rightarrow {}^4E_g(G)$
		360	$^6A_{1g} \rightarrow {}^4T_{2g}(D)$
		340	$^6A_{1g} \rightarrow {}^4E_g(D)$
Co(II)	5.20	820	$^4T_{1g}(F) \rightarrow {}^4E_g$
		475	$^4T_{1g}(F) \rightarrow {}^4T_{1g}$ P)
Ni(II)	3.19	900	$^3A_{2g} \rightarrow {}^3T_{2g}$
		650	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$
		400	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$
Cu(II)	1.80	500	$^2E_g \rightarrow {}^2T_{2g}$

The complexes lose ligand water at 220-240° ; the loss corresponds to calculated amount for dihydrates. These decompose at high temperatures, the order of thermal stability being Cd(460°) > Zn(420°) > Co(400°) ≈ Ni(400°) > Mn(360°) > Cu(300°). This is in good agreement with the assumption that half-filled d^5 and completely-filled d^{10} metal complexes are more stable[12], however, Mn(II) does not follow this rule. The residues do not conform to the metal oxide alone indicating that the organic part does not volatilize completely even at 800°.

The molecular weights of these metal chelates could not be ascertained for lack of their solubility in common organic solvents. The extreme insolubility and the high thermal stability of the complexes suggest their polymeric nature.

Acknowledgement

The financial support received from the Ministry of Defence, Government of India, for the project and the award of a Research Fellowship to BS are gratefully acknowledged. Thanks are also due to the Council of Scientific and Industrial Research, New Delhi for the award of a Senior Research Fellowship to VB.

References

1. P. L. MAURYA, B. V. AGARWALA and A. K. DEY, *Inorg. Nuclear Chem. Lett.*, 1977, 13, 145 ; *Indian J. Chem.*, 1978, 16A, 358 ; *Rev. Chim. Minérale*, 1978, 15, 501 ; *Polymer Bull.*, 1979, 1, 631 ; *J. Indian Chem. Soc.*, 1978, 55, 418.
2. V. BANERJIE and A. K. DEY, *Makromol Chem.*, 1979, 180, 2133 ; *Polymer Bull.*, 1979, 1, 685 ; XXth Intl. Conf. on *Coord. Chem.*, Calcutta, (December 1979) I, 126, p. 211.
3. L. PAULING, The Nature of Chemical Bond, Oxford University Press, London, 1959.
4. D. HADZI and M. PINTAR, *Spectrochim. Acta*, 1959, 8, 249.
5. A. N. SPECA, L. S. GELFAND, L. L. PUTLEWSKI, C. OWENS and N. M. KARAYANNIS, *Inorg. Chem.*, 1976, 15, 1493.
6. K. NAKAMOTO, Infrared Spectra of Inorganic and Coordination Compounds, Wiley-Interscience, New York, 1975.

7. H. H. FREEDMAN, *J. Amer. Chem. Soc.*, 1961, 83, 2900.

8. D. SUTTON, Electronic Spectra of Transition Metal Complexes, McGraw-Hill, London, 1968.

9. J. LEWIS, F. E. MABBS and H. WINGOLD, *J. Chem. Soc.*, (A) 1968, 1699.

10. R. S. DRAGO, Physical Method in Inorganic Chemistry, Reinhold, New York, 1965.

11. I. M. PROCTER, B. J. HATHWAY and P. NICHOLLS, *J. Chem. Soc.* (A), 1968, 1678.

12. S. W. HOROWITZ and T. P. PERROS, *J. Inorg. Nuclear Chem.*, 1964, 26, 139.

J. Indian Chem. Soc.,
Vol. LVII, April 1980, pp. 368-371

Substituted Carbonyl Complexes of Rhodium Containing Amino Acidato Ligands*

DULAL DOWERAH and M. M. SINGH**

Department of Chemistry, Dibrugarh University, Dibrugarh-786 004, Assam, India

Manuscript received 2 November 1979, accepted 28 December 1979

The reactions of halogen, gaseous haloacids, alkyl and aryl amines, 2-2′ bipyridyl, 1-10 phenanthroline, tetracyanoethylene on the dicarbonyl amino acidato complexes $Rh(CO)_2LL'$ and monocarbonyls RhCO(LL′)L, where LL′ = amino acedato groups and L = PPh_3 have been reported. The reaction of gaseous haloacids on the dicarbonyls produces $[Rh(CO)_2X]_2$ and free amino acids. 1-10 phenanthroline and 2-2′ bipyridyl react with the dicarbonyls giving products where both CO groups have been substituted. Chlorination of the monocarbonyl derivatives produce the oxidised products of Rh(III) with a sharp CO absorption bands at ca. 2110 cm^{-1}. Tetracyanoethylene adds to the dicarbonyls giving $Rh(CO)_2(LL')TCNE$. Monodentate nitrogen donor ligands substitutes the cis carbonyls giving $Rh(LL')(RNH_2)_2$. The complexes are characterised by elemental analyses, conductivity measurements, IR and UV-VIS spectra.

Apart from catalytic activity, recent investigations show that rhodium compounds exhibit marked tendency to act as antibacterial and antitumor agents[1-3]. Indeed, some neutral Rh(I) complexes having overall square planar geometry do resist the growth of certain tumor by selectively inhibiting the leucine and uridine incorporation into protein[2]. We have found that $Rh(CO)_2LL'$ complexes (LL′ = glycinato, L-leucinato, L-alaninato and L-phenylalaninato groups) demonstrate significant activity in arresting the growth of certain bacterium with substantial filamentous growth in *E. coli*[3]. In fact, dicarbonyl leucinatorhodium(I) has been put to antitumor study in National Cancer Institute, USA. It would therefore be interesting to study the behaviour of these amino acidato complexes of Rh(I) (specially of leucinato derivatives) towards some organic amines, TCNE, halogens and N-heterocyclic ligands.

Results and Discussion

Action of monodentate and bidentate nitrogen donor ligands on the dicarbonyls :

Out of the various amines used (methyl amine, ethyl amine, isobutyl amine and cyclohexyl amine) $Rh(CO)_2LeuO$ forms stable yellow compounds with only isobutyl and cyclohexyl amine. These products are neutral (conductivity data) and correspond to the molecular formula $Rh(LeuO)(RNH_2)_2$ (R = isobutyl and cyclohexyl groups). The parent dicarbonyl shows split νCO bands in the region 2115-1970 cm^{-1} whereas the amine substituted products did not absorb in this region. The relatively broad absorption bands in the region 3400 and 3200 cm^{-1} have been assigned to νNH on the basis of the well established literature data[4]. Similarly the region around 1600 cm^{-1} is relatively less resolved due to the overlapping of $\nu_{As}COO$ and three δNH_2 bands. In the parent compounds, however, these bands appear as distinct absorptions. The UV-VIS spectra of the amine substituted compounds exhibit broad absorption bands in the near ultraviolet region with absorption maxima at 35,500 cm^{-1} (E = 9000) in the cyclohexyl compound and at 32,500 cm^{-1} (E = 9000) for the isobutyl amine compound. These bands may be attributed to the MLCT bands as observed for other Rh(I) complexes[5-6].

The action of 1-10 phenanthroline and 2-2′ bipyridyl (N – N) on $Rh(CO)_2LeuO$ produce dark green and brown hygroscopic products which show no CO bands. The analytical data of the complexes conform to their molecular formula Rh(LeuO)(N – N). The UV-VIS spectra exhibit relatively broad band at ca. 28,000 cm^{-1} and an unresolved band at ca. 31,000 cm^{-1} characteristic of Rh(I) compounds[5-6]. From these data and from the non-conducting nature of the compounds it appears that these compounds are most probably square planar. These results indicate that the cis CO groups can be replaced by nitrogen donor ligands keeping the metal in the same oxidation state which is of great practical importance in bio-inorganics[2].

Action of tetracyanoethylene on the dicarbonyls :

When a solution of TCNE in benzene is added to a solution of the dicarbonyls in 1 : 1 mole ratio, the yellow solution immediately turns red which on

* This paper was presented at the Convention of Chemists, Kurukshetra University, 1979.
** Author to whom all correspondence should be made.

keeping overnight gives either brilliant blue green or brown yellow products. The TCNE adducts exhibit two distinct sharp carbonyl bands (ca. 2090 and 2020 cm^{-1}) due to two cis CO groups instead of much split bands as observed in parent dicarbonyls. The characteristic CN band of TCNE is found at ca. 2220 cm^{-1}. These adducts might exist as either trigonal pyramidal (with TCNE occupying the apex) or quasioctahedral compounds containing "metal cyclopropane ring"[7,8,9]. This type of adduct formation of TCNE to other square planar Rh(I) complexes have been reported[9-10]. The leucinato complex shows a broad band in UV-VIS spectra with absorption maxima at ca. 30,000 cm^{-1} and three poorly resolved absorption maxima at ca. 16,000 cm^{-1}. The other products containing glycinato and phenylalaninato groups show similar absorption bands but only in the higher wave length region. Thus in these compounds a broad band is observed at ca. 45,000 cm^{-1} which has a tendency to split and two poorly resolved bands around 26,000 cm^{-1}. These bands *indicate* that Rh(I) is probably oxidised to Rh(III). Moreover, the unsymmetrical appearance (twin structure) of the bands at ca. 26,000 cm^{-1} may be due to the distortion of the quasioctahedral structure. Further in TCNE itself a strong band appears at 40,000 cm^{-1} due probably to molecular π-transitions which is either absent in the TCNE derivatives or appears as a very weak absorption. This probably indicated that TCNE is bonded to the central metal atom through the involvement of the C=C.

Action of chlorine on substituted monocarbonyls :

When dry chlorine is passed through a suspension of Rh(CO) (LL')L_2 in CCl_4 the compounds go into solution finally forming the reddish yellow product RhCOL(LL')Cl_3. The compounds show a νCO peak at ca. 2100 cm^{-1}. The increased νCO value from 1965 cm^{-1} (parent compounds) to 2100 cm^{-1} is characteristic of carbonyl complexes of Rh(III)[11-13]. The compounds contain about three chlorine atoms per rhodium atom. To account for this and to preserve 18 electron rule for Rh(III) carbonyl derivatives we invoke the idea of amino acidato ligands undergoing chlorine substitution. This type of halogenation of quinoline-8-olato group in Rh(Oxq) $(CO)_2$ when treated with halogen has been reported[14]. It is also found from NMR studies that the methylene groups in glycinato type of ions become activated upon chelation and in fact the substitution of methylene proton of coordinated amino acidato groups in Copper(II) and Cobalt(III) complexes have been reported[15-18]. Therefore in Rh(CO)L(R-C*H*(NH_2)COO)Cl_2 it is probable that one of the three chlorines displaces the proton of the activated methylene group (alkyl substituted for the above case) thus suggesting the formula Rh(CO)-L(R-CCl(NH_2)COO)Cl_2. The chloro substituted methylene group will obviously influence the position of ν_{As}COO which is actually observed in the shifts of these absorptions to higher region (see Table 1).

Action of HX on the dicarbonyls :

Previously[19] we reported that gaseous HCl reacts with the dicarbonyls producing the parent dimer with the simultaneous release of free amino acids which is a reversible process. Now it is found that when fumes of HBr is passed over any of the solid amino acidato dicarbonyls, the bromobridged dimer is produced which is an easy method for the preparation of the bromobridged dimer from the chloro bridged one via the amino acidato derivatives. These results are in agreement with those of Burlex *et al.*[20] who have shown that HX (X=Cl or Br) reacts with the square planar Rh(I) complexes Rh(acac)COL (L=PPh_3 or $AsPh_3$) to give

TABLE 1—IMPORTANT IR AND UV-VIS SPECTRAL DATA OF THE RHODIUM COMPOUNDS

Compound	E_{max} in μm^{-1}	Extinction coefficient M^{-1} cm^{-1} (principal band)	νCO cm^{-1}	νCN cm^{-1}	νNH cm^{-1}	ν_{As}COO cm^{-1}	δNH_2 cm^{-1}
$Rh(CO)_2$(GlyO)TCNE	4.8, 2.7, 2.55	8289	2085s 2010s	2200s	3200- 3100br	1625- 1600br	
$Rh(CO)_2$(PheO)TCNE	4.75, 2.65, 2.55	7014	2080s 2015s	2220s 2165sh	3300br	1600br	
$Rh(CO)_2$(LeuO)TCNE	3.0, 1.67, 1.57, 1.4	6012	2090s 2020s	2225s	3200br	1650br	1600br
Rh(LeuO)(Cha)	3.55	9175	—	—	3350br 3200br	1625- 1575br	
Rh(LeuO)(Iba)	3.25	9050	—	—	3300- 3200br	1600br	
$RhCOPPh_3$(LeuO-Cl)Cl_2	—	—	2105s	—	3400br 3200br	1625br*	1575br
$RhCOPPh_3$(PheO-Cl)Cl_2	—	—	2104s	—	3350br	1625br*	1565br
$RhCOPPh_3$(TrpO-Cl)Cl_2	—	—	2107s	—	3350br 3150br	1725br*	1610br

GlyO=glycinato, PheO=L-phenylalaninato, LeuO=L-leucinato, TrpO=L-tryptophanato, s=sharp, br=broad, sh=shoulder.

* For the respective parent compounds the A_sCOO are at 1610, 1605 and 1670 cm^{-1} respectively.
Cha=cyclohexyl amine, Iba=isobutyl amine.

the halobridged dimer $[RhXCOL]_2$ and of Ukhin *et al.*[21] who have also established that $Rh(CO)_2L$(HL = acetylacetone) reacts with HLL(HLL = CF_3COOH, $C(CH_3)_2FCOOH$, HCN) to give $[Rh(CO)_2LL]_2$.

Experimental

The parent compounds were prepared following published methods[19,22]. The important IR and UV-VIS spectral bands of the reported compounds are given in Table 1.

$Rh(LL')(RNH_2)_2$: An acetone solution of 0.1 g of the dicarbonyl $Rh(CO)_2$LeuO was treated with excess of the amines. The solution was kept for one week in vacuum which on evaporation under reduced pressure gave yellow products.

Leucinatobis (cyclohexyl amine) rhodium(I) : RhLeuO(Cha)₂ :

Yellow compound. (Found Rh, 23.4 ; C, 41.4 ; H, 8.5 ; N, 9.4 ; Calc. for $RhC_{18}H_{38}N_3O_2$: Rh, 23.8 ; C, 41.1 ; H, 8.8 ; N, 9.7%).

Leucinatobis (isobutyl amine) rhodium(I). RhLeuO(Iba)₂ :

Yellow compound. (Found : Rh, 23.4 ; C, 44.0 ; H, 8.5 ; N, 10.9 ; Calc. for $RhC_{14}H_{34}N_3O_2$: Rh, 23.8 ; C, 44.3 ; H, 8.9 ; N, 11.08%).

$Rh(CO)_2(LL')$TCNE : A solution of TCNE in benzene was treated with a solution of amino acidato dicarbonyls in 1 : 1 mole ratio. The solution was kept overnight for complete reaction. Evaporation of the solution under vacuum gave yellow brown to brilliant blue green compounds. The compounds are soluble in chloroform or alcohol.

$Rh(CO)_2$(GlyO)TCNE : Yellow brown amorphous compound. (Found : C, 32.5 ; H, 1.15 ; N, 19.1 ; Calc. for $RhC_{10}H_4N_5O_4$: C, 33.2 ; H, 1.1 ; N, 19.3%).

$Rh(CO)_2$(PheO)TCNE : Brown crystalline compound. (Found : C, 45.0 ; H, 2.0 ; N, 15.2 ; Calc. for $RhC_{17}H_{10}N_5O_4$: C, 45.2 ; H, 2.2 ; N, 15.5%).

$Rh(CO)_2$(LeuO)TCNE : Brilliant blue green crystal. (Found : C, 39.6 ; H, 2.9 ; N, 16.4 ; Calc. for $RhC_{14}H_{12}N_5O_4$: C, 40.2 ; H, 3.07 ; N, 16.7%).

$Rh(CO)L(LL'\text{-}Cl)Cl_2$: A stream of dry chlorine gas was passed through a suspension of 0.1 g of the monocarbonyls $RhCO(LL')L_2$ in CCl_4 for one hour. The compound dissolves and a reddish precipitate slowly separated from the solution. Filtered, washed with chloroform and finally dried.

$Rh(CO)PPh_3$ (LeuO-Cl)Cl_2 : Yellow compound. (Found : C, 47.3 ; H, 4.1 ; N, 2.1 ; Cl, 15.0 ; Calc. for $RhC_{25}H_{27}NCl_3PO_3$: C, 47.7 ; H, 4.3 ; N, 2.2 ; Cl, 15.2%).

$Rh(CO)PPh_3$(TrpO-Cl)Cl_2 : Yellow compound. (Found : C, 50.8 ; H, 3.9 ; N, 3.7 ; Cl, 14.8 ; Calc. for $RhC_{30}H_{26}N_2Cl_3PO_3$: C, 51.2 ; H, 4.1 ; N, 3.9 ; Cl, 15.1%).

$Rh(CO)PPh_3$ (PheO-Cl)Cl_2 : Reddish compound. (Found : C, 50.6 ; H, 3.77 ; N, 1.9 ; Cl, 15.6 ; Calc. for $RhC_{28}H_{24}NCl_3PO_3$: C, 50.6 ; H, 3.77 ; N, 2.1 ; Cl, 15.9%).

Rh(LeuO)(N-N) : To an acetone solution of 0.1 g of the dicarbonyl $Rh(CO)_2$LeuO was added solid 1-10 phenanthroline or 2-2' bipyridyl (N-N) in 1 : 1 mole ratio. An immediate separation of solid dark green to brown products took place with evolution of CO gas. Filtered and washed with acetone on filter, collected and preserved under vacuum.

L-Leucinatophenanthrolinerhodium(I) ; Rh(LeuO)-Phen :

Dark green hygroscopic product. (Found : C, 51.5, H, 4.2; Rh, 24.2; Calc. for $RhC_{18}H_{20}N_3O_2$: C, 52.3 ; H, 4.8 ; Rh, 24.8%).

L-Leucinatobipyridylrhodium(I) : Rh(LeuO)-BIpy :

Brown hygroscopic product. (Found : C, 48.6 ; H, 5.1 ; Rh, 26.0 ; Calc. for $RhC_{16}H_{20}N_3O_2$: C, 49.5 ; H, 5.1 ; Rh, 26.5%).

Acknowledgement

Both the authors are thankful to UGC, India for a research fellowship to DD and for a research grant to MMS.

References

1. R. J. BROMFIELD, R. H. DAINTY, R. D. GILLARD and B. T. HEATON, *Nature*, 1969, **223**, 735.
2. T. GIRALDI, G. EAVA, G. BERTOLI, G. MESTRONI and G. ZASSINOVICH, *Cancer Res.*, 1977, **37**, 2662.
3. D. DOWERAH, M. M. SINGH and B. GOGOI, *J. Inorg. Nuclear Chem.*, (Bio Inorganic Section), in press.
4. K. NAKAMOTO, "Infrared Spectra of Inorganic and Coordination Compounds", John Wiley and Sons., N Y., 1970.
5. R. BRADY, B. R. FLYNN, G. L. GEOFFROY, H. B. GRAY, J. PEONE, Jr. and L. VASKA, *Inorg. Chem.*, 1976, **15**, 1485.

6. G. L. GEOFFROY, H. ISCI, J. LITRENI and W. R. MASON, *Inorg. Chem.*, 1977, **16**, 1950.

7. W. H. BADDLEY, *J. Amer. Chem. Soc.*, 1966, **88**, 4545.

8. YU. S. VARSHAVSKII, T. G. CHERKASOVA, M. M. SINGH and N. A. BUZINA, *Russ. J. Inorg. Chem.*, 1970, **15**, 1427.

9. W. H. BADDLEY, *J. Amer. Chem. Soc.*, 1968, **90**, 3705.

10. D. STROPE and D. F. SHRINER, *Inorg. Chem.*, 1974, **13**, 2652.

11. K. GOSWAMI and M. M. SINGH, *J. Indian Chem. Soc.*, 1979, **56**, 477.

12. M. A. BANNET, R. J. H. CLARK and D. L. MILLNER, *Inorg. Chem.*, 1967, **6**, 1647.

13. M. M. SINGH and YU. S. VARSHAVSKII, *Zh. Neorg. Khim.*, 1969, **14**, 2434.

14. YU. S. VARSHAVSKII, T. G. CHERKASOVA and N. A. BUZINA, *Russ. J. Inorg. Chem.*, 1972, **17**, 1150.

15. R. D. GILLARD and D. A. PHIPPS, *Chem. Commun.*, 1970, 800.

16. P. M. HARRISON and R. D. GILLARD, *J. Chem. Soc.*, A, 1967, 1657.

17. M. MUAKAMI and K. TAKAHASHI, *Bull. Chem. Soc.*, Japan, 1959, **32**, 308.

18. A. NAKAHARA, S. NISHIKAWA and J. MITANI, *Bull. Chem. Soc.*, Japan, 1967, **40**, 2212.

19. D. DOWERAH and M. M. SINGH, *J. Chem. Research* (S), 1979, **38**, (M) 258.

20. D. M. BURLEX, M. J. HACKER and R. D. W. KEMMITT, *J. Organometal. Chem.*, 1972, **43**, 425.

21. YU. L. UKHIN and YU. A. SHVETOSV, *Izv. Akad. Nauk, SSSR. Ser. Khim.*, 1972, **7**, 1653.

22. D. DOWERAH and M. M. SINGH, *Trans. Met. Chem.*, 1976, **1**, 294.

J. Indian Chem. Soc.,
Vol. LVII, April 1980, pp. 372-373

Mixed Ligand Anionic Complexes of Nickel(II)

BIPIN B. MAHAPATRA, A. PANDA and S. K. PUJHARI

Department of Chemistry, Panchayat College, Bargarh, Sambalpur

and

S. GURU

Department of Chemistry, Ravenshaw College, Cuttack (Orissa)

Manuscript received 16 November 1979, accepted 20 December 1979

Tetrathiocyanato Nickel(II) complex was reacted with a number of nitrogen donor ligands and a sulfur donor ligand and complexes of the composition $[Ni(NCS)_4L_2]$ where L is pyridine, γ-picoline, quinoline, iso-quinoline, 2,6 lutidine, diethylamine, quinaldine, piperidine, $[Ni(NCS)_4L]$ where L is ethylenediamine, o-phenylenediamine and $[Ni(NCS)_2L]$ where L is oxine and piperidyldithiocarbamate were isolated. These have been characterised on the basis of analysis, conductance, magnetic susceptibility, IR and electronic spectral studies.

A number of simple and mixed ligand anionic complexes of Nickel(II) have been reported[1] of the composition $[QH]_2[NiX_4]$ where QH is a quaternary halide and tetrahedral configuration has been suggested for them. Also complexes of the composition $[MLX_3]^-$ where M is a bivalent metal like Co(II), Ni(II) or Zn(II) and X is Cl^-, Br^-, I^- and L is a nitrogen, phosphorous or arsenic ligand have been prepared[2,3] earlier and established as tetrahedral compounds. Even though $[Ni(NCS)_4]^{--}$ has been long since known as a tetrahedral species, little work has been done to change the stereochemistry of these complexes by reacting with other nitrogen, oxygen and sulfur ligands. To increase the coordination number, particularly to synthesise compounds of co-ordination number five, we have been trying[4] to synthesise anionic mixed ligand complexes starting from these types of tetrahedral compounds. In this communication we report a number of hexa-coordinated and two penta-coordinated mixed ligand anionic (thiocyanate) complexes using different ligand donor atoms.

Experimental

All the chemicals used were of AnalaR grade. An ethanolic solution of nickel thiocyanate was treated with an ethanolic solution of tetramethylammonium thiocyanate in 1 : 2 proportion when green crystalline compound of ditetramethylammonium tetrathiocyanato-nickel(II) was separated out. This was then filtered, washed with ethanol and dried in vacuo.

The mixed ligand complexes were prepared by adding requisite amount (1 : 2 ratio) of ligands separately to ethanolic suspension of ditetramethylammonium tetrathiocyanato-nickel(II) and refluxing for about 30 minutes. On cooling, crystalline compounds separated out which were then filtered, washed with ethanol followed by ether and dried in vacuo.

Discussion

On the basis of analysis and conductance data, the complexes have the composition $[Me_4N]_2[Ni(NCS)_4L_2]$ where L is pyridine, γ-picoline, quinoline, isoquinoline, quinaldine, piperidine, 2,6 lutidine, diethylamine, $[Me_4N]_2[Ni(NCS)_4L]$ where L is ethylenediamine, o-phenylenediamine and $[Me_4N]_2[Ni(NCS)_3L]$ where L is oxine and piperidyldithiocarbamate. All the complexes are light blue, green or violet crystalline compounds, soluble in acetone, in which medium the Λ_M values are around 250 mhos cm^2 indicating 2 : 1 electrolytic nature of the complexes. Magnetic susceptibility measurements indicate the presence of two unpaired electrons and the μ_{eff} values are characteristic of spin-free octahedral complexes except with oxine and piperidyldithiocarbamate. The magnetic moment values of these complexes are quite low (Table 1).

In the infrared spectra, absorption bands are noticed at 760 (s), 950 (vs) and 1490 (vs) cm^{-1}, characteristic of the tetramethylammonium ion, modified due to complexation. Very sharp absorption bands are absorbed ~2060 cm^{-1} attributable to ν(C≡N) of thiocyanate. In addition, ν(C=S) and ν(C–O) bands have been observed at 1235 and 1200 cm^{-1} for the thiocarbamate and oxine complexes respectively. In case of oxine complex, ν(O–H) has disappeared indicating co-ordination of the oxine molecule through the hydroxyl oxygen. Most of the absorption bands due to free nitrogen, oxygen

TABLE 1—COLOUR, ANALYSIS, CONDUCTANCE, MAGNETIC SUSCEPTIBILITY AND IR SPECTRAL DATA

Compound	Colour	%Nickel		%SCN		%Nitrogen		AM	μ_{eff}		
		Found	Reqd.	Found	Reqd.	Found	Reqd.	mhos cm²	B.M.	ν(C≡N)	ν(M–N)
$[L]_2[Ni(SCN)_4]$	Blue	12.97	13.10	51.62	52.87	16.74	16.86	240	2.9	2065	385, 360
$[L]_2[Ni(SCN)_4PY_2]$	Bluish violet	9.68	9.83	33.54	33.87	18.65	18.73	238	3.1	2060	375, 360
$[L]_2[Ni(SCN)_4(\gamma\text{-pic})_2]$	Violet	9.24	9.38	36.89	37.18	17.62	17.92	2.30	3.1	20.70	380, 360
$[L]_2[Ni(SCN)_4Q_2]$	Bluish violet	8.29	8.42	33.07	33.29	15.91	16.06	230	2.9	20.60	370, 360
$[L]_2[Ni(SCN)_4IQ_2]$	Light violet	8.37	8.42	33.14	33.29	15.87	16.06	245	3.0	20.70	390, 360
$[L]_2[Ni(SCN)_4Qn_2]$	Blue	7.92	8.10	31.94	32.16	15.18	15.45	236	3.2	2070	380, 360
$[L]_2[Ni(SCN)_4(2,6\ lut)_2]$	Green	8 87	8.99	35.27	35.54	17.24	17.45	240	3.1	2055	385, 360
$[L]_2[Ni(SCN)_4(pip)_2]$	Light yellow	9.53	9.64	37.86	38.11	18.16	18.39	225	2.9	2065	380, 360
$[L]_2[Ni(SCN)_4(DEA)_2]$	Green	9.96	10.04	39.32	39.69	19.08	19.32	230	3.0	2060	390, 360
$[L]_2[Ni(SCN)_3Pdtc]$	Olive green	10.58	10.58	32.04	32.17	15.27	15.53	1.98	2.0	2070	385, 260 (M–S)
$[L]_2[Ni(SCN)_3Oxine]$	Light green	10.94	11.16	32.88	33.11	15.68	15.97	235	2.2	2070	390, 450 (M–O)
$[L]_2[Ni(SCN)_4en]$	Green	15.28	15 34	29.97	30.30	28.94	29.23	240	2.9	2060	370, 350
$[L]_2[Ni(SCN)_4o\text{-}PhDA]$	Violet	13.51	13.64	26.63	26.9	26.05	26.26	245	3.1	2070	380, 350

L = Me_4N^+ cation, Py = Pyridine, γ-pic = γ-picoline, Q = Quinoline, IQ = I-soquinoline, Qn = quinaldine, 2.6-lut 2,6-lutidine, Pip = piperidine, DEA = Diethylamine, Pdtc = Piperidyl dithiocarbamate, en = ethylenediamine, o-PhDA = o-Phenylenediamine.

and sulfur ligands have been modified due to bonding with the metal ion. Evidence for the co-ordination of the bases have been further substantiated by appearance of bands ~ 350-390 cm^{-1} in the low frequency region assignable[5] to ν(M – N). In addition, for the oxine and dithiocarbamate complex ν(M – O) and ν(M – S) appear ~ 460 and ~ 260 cm^{-1} respectively.

In the electronic spectra of the complexes with nitrogen ligands, three absorption bands are observed around 9-9.5, 11-13, 24-26 k.k. region attributable to the three characteristic transitions of Nickel(II) ion in an octahedral[6,4] environment. The low molar absorptivity values are also in conformity with this formulation. Complexes with oxine and piperidyldithiocarbamate have two absorption bands ~ 25.5 and ~ 20.2 k.k. region, attributable to $^3B_1 \rightarrow {}^3E''$ and $^3B_1 \rightarrow {}^3E'$, transitions. This is in conformity with earlier reports on pentacoordinated complexes of Nickel(II)[7-9]. The magnetic moment values are also low which supports the configuration predicted by electronic spectra. Hence these two complexes are presumably pentacoordinated. However, X-ray crystallography study will reveal the exact stereochemistry of the complexes.

References

1. N. S. GILL and R. S. NYHOLM, *J. Chem. Soc.*, 1959, 3907.
2. D. H. BROWN and K. P. FORREST, R. H. NUTTAL and W. A. SHARP, *J. Chem. Soc.*, (A), 1968, 2146.
3. W. DE. W. HORROCKS (Jr), J. H. TEMPLETON and A. ZALKIN, *Inorg. Chem.*, 1968, 7, 2303.
4. BIPIN B. MAHAPATRA, B. K. MAHAPATRA and S. GURU *J. Indian Chem. Soc.*, 1978, 55, 513.
5. J. R. FERRARO, "Low Frequency Vibrations of Inorganic and Co-ordination Compounds"—Plenum Press, New York, 1971.
6. A. B. P. LEVER, "Inorganic Electronic Spectroscopy". Elsevier Amsterdam, 1968.
7. W. S. J. KELLY, G. H. FORD and S. M. NELSON, *J. Chem. Soc.* (A), 1971, 388.
8. W. V. DAHLHOFF and S. M. NELSON, *J. Chem. Soc.*, (A), 1971, 2184.
9. M. CIAMPOLINI, J. GELZOMINI and N. NANDI, *Inorg. Chim. Acta*, 1968, 2, 343.

J. Indian Chem. Soc.,
Vol. LVII, April 1980, pp. 374-377

Studies on Th(IV) and Zr(IV) Complexes of Oxygen Donor Ligands. Part XII. Oxozirconium(IV) Complexes of 2-methyl pyridine N-oxide*

R. K. AGARWAL**, P. C. JAIN, MAHESH SRIVASTAVA and A. K. SRIVASTAVA†

Department of Chemistry, Meerut College, Meerut-250 001 (India)

and

T. N. SRIVASTAVA

Department of Chemistry, Lucknow University, Lucknow

Manuscript received 16 November 1979, accepted 22 December 1979

A new series of five and seven coordinate complexes of oxozirconium(IV) of the type $ZrO(picO)_4X_2$($X=Cl$, Br, NO_3 or NCS) and $ZrO(picO)_4X_2$($X=ClO_4$ or I), (where picO = 2 methyl pyridine N-oxide) have been synthesised and characterised by conventional technique including far i.r. In all the complexes picO is bonded through the lone oxygen atom. Thermal behaviour of the complexes has also been investigated.

RECENTLY a large number of coordination compounds of pyridine N-oxide (PYO) and its ring substituted derivatives with a wide variety of metal salts have been synthesised and characterised[1-3]. Pyridine N-oxide and its 3- or 4-substituted derivatives do not introduce steric effects during coordination to metal ions[1]. In the cases of 2- or 2,6-substituted pyridine N-oxides, steric factors become important in stabilization of complexes[4-6]. However, in the case of oxozirconium(IV) complexes of 2,6-dimethylpyridine N-oxide, the steric repulsion between the two ligand groups is less severe because of the large ionic radius of the metal ion[6,7]. Comparatively very little is known about the compounds of oxozirconium(IV) with aromatic amine N-oxide[7-12]. The present paper deals with the synthesis and characterisation of complexes of 2-methyl pyridine N-oxide (picO) with oxozirconium(IV) salts.

Experimental

Materials employed $ZrO(NO_3)_2.5H_2O$ and $ZrOCl_2.4H_2O$ were obtained from B.D.H. Anhydrous $ZrOCl_2$ prepared as reported earlier[13]. Crystalline zirconyl perchlorate was prepared by established method[14]. Other zirconyl halides were prepared as follows : Methanolic solutions of anhydrous $ZrOCl_2$ and KX (X=Br, I, SCN) were mixed in 1 : 2 equimolar ratio and stirred the reaction mixture on a magnetic stirrer for 0.5h. The precipitated KCl was filtered off and filtrate containing $ZrOX_2$ was used for the preparation of the complexes.

2-Methyl pyridine N-oxide was obtained from Aldrich Chemical Company, Inc., U.S.A.

Preparation of the Complexes :

A solution of oxozirconium salt in methanol was treated with an excess of the picO, in the same solvent. The mixture was refluxed on waterbath for *ca.* 3h and the excess solvent was removed by distillation. The residual mass on treatment with diethyl-ether yielded a crystalline solid which was filtered off, washed several times with solvent ether and dried under vacuum over anhydrous $CaCl_2$.

Analysis :

The metal content of the complexes was determined as earlier[8]. The perchlorate was determined by the method of Kurz[15]. The halide in the complexes was determined by Volhard's method, while the thiocyanate was determined by titration of a slightly acidic solution of the complex against standard silver-nitrate.

The electrical conductance measurements of the complexes were carried out with a Toshniwal conductivity bridge at room-temperature. The molecular weight of the complexes was determined cryoscopically in freezing nitrobenzene. The i.r. spectra of the complexes were recorded in the 4000-200 cm^{-1} range using Perkin-Elmer infrared spectrophotometer model 521 and Beckmann I.R.-12. The d.t. a. were

* Presented at the 46th Annual Session of National Academy of Sciences (India) on Oct. 27-29, 1979, Nagpur University, Nagpur.
** On leave from L. R. Post-Graduate College, Sahibabad (Ghaziabad).
† Author for correspondence.

TABLE 1—ANALYTICAL CONDUCTIVITY AND MOLECULAR WEIGHT DATA OF OXOZIRCONIUM IV) COMPLEXES OF 2-METHYL-PYRIDINE-N-OXIDE

Complex	Colour	Zr% Found (Calcd)	C% Found (Calcd)	N% Found (Calcd)	H% Found (Calcd)	Anion% Found (Calcd)	Am ohm^{-1} cm^2 $mole^{-1}$ in $PhNO_2$	in DMSO	Electrolytic nature	Mol. wt. Found (Calcd)
$ZrOCl_2.2picO$	Light yellow	22.39 (22.97)	36.18 (36.36)	7.28 (7.07)	3.47 (3.53)	17.80 (17.92)	2.8	10.9	Non-electrolytic	372 (396)
$ZrOBr_2.2picO$	Grey	18.54 (18.76)	29.24 (29.69)	5 98 (5.77)	2.67 (2.88)	32.42 (32.98)	1.7	9.3	Non-electrolytic	467 (485)
$ZrOI_2.4picO$	Brown	11.20 (11.41)	35.90 (36.13)	7.42 (7.02)	3.32 (3.51)	31.10 (31.66)	49.7	78.7	1 : 2	257 (797)
$ZrO(ClO_4)_2.picO$	Reddish yellow	11.98 (12.26)	39.01 (38.81)	7.32 (7.54)	3.42 (3.77)	26.10 (26.82)	51.3	83.9	1 : 2	230 (742)
$ZrO(NO_3)_2.picO$	Creamish	19.98 (20.26)	32.32 (32.07)	12.26 (12.47)	3.40 (3.11)	— (27.61)	2.3	9 8	Non-electrolytic	417 (449)
$ZrO(NCS)_2.2picO$	Muddy	38.67 (20.63)	12.43 (38.09)	12.43 (12.69)	3.37 (3.17)	25.90 (26.30)	1.6	8.6	Non-electrolytic	423 (441)

carried out in air atmosphere using DTA-02. Universal (DDR) using alumina as reference substance and the heating rate was 10° min^{-1}, while t.g.a. were done on Cahn R.G.-Electrobalance with platinum boat in static air and the heating rate was 6° min^{-1}.

Results and Discussion

The interaction of oxozirconium(IV) salts with 2-picO results in the formation of $ZrO(picO)_2X_2$ ($X = Cl,Br,NO_3,NCS$) and $ZrO(picO)_4X_2$ ($X = ClO_4,I$). Analysis of the complexes are given in Table 1. The complexes have high melting points and sufficiently soluble in polar solvents and insoluble in non-polar solvents. The molar conductance-values in nitrobenzene and sulphoxide indicate that the chloro, bromo, nitrato and thiocynato. Complexes are non-electrolytes while the iodo and perchlorato complexes behave like 1 : 2 electrolyte. The molecular weight determination of the complexes also support the same electrolytic nature of the complexes. The types of the complexes isolated during the present study have 1 : 2 or 1 : 4 stoichiometry with different oxozirconium(IV) salts. Previous workers[7,8] have shown that with PyO and LNO formed complexes of 1 : 2, 1 : 4 and 1 : 6 stoichiometry with different oxozirconium salts. A comparison of the nature of the three ligands with oxozirconium(IV) salts. Thus clearly indicates the steric hindrance introduced in the complex formation by the presence of the 2-methyl substituent in picO.

Infrared Studies :

In coordination of the amine-oxide to a metal ion through the NO oxygen generally influenced. The three main vibration frequencies, (NO stretching vibration, NO bending vibration and C – H ring out-of-plane deformation) of amine oxides[16].

In the spectra of the free picO the NO stretching vibration appears as a strong band at 1245 cm^{-1} [17,18] in nujol-mull while at 1265 cm^{-1} in KBr[19], which suffers a significant negative shift on complexation with oxozirconium(IV) salts (Table 2). The decrease in the frequency of the NO stretching vibration is attributed to coordination from the oxygen atom of the base causing a decrease in π character of the N – O bond[16,20].

TABLE 2—PERTINENT I.R SPECTRAL DATA (cm^{-1}) OF ZrO(IV) COMPLEXES OF 2-picO

Complex	γ(NO)	δ(NO)	γCH out-of-plane deformation	γ(MO)
$ZrOCl_2.2picO$	1220s	810m	800s, 780s	382m
$ZrOBr_2.2picO$	1218m	820m	800s, 755s	380m
$ZrOI_2.4picO$	1215s	820m	790s, 755s	385m
$ZrO(ClO_4)_2.4picO$	1220s	815m	790m, 780m	390m
$ZrO(NO_3)_2.2picO$	1210m	810m	795s, 760m	400m
$ZrO(NCS)_2.2picO$	1220s	810m	790s, 780m	390m

An absorption of strong intensity at 845 cm^{-1} [19] has been assigned to NO bending mode and from the tabulated data, it is apparent that only a slight shift of this vibration is observed on complexation[19]. Absorption associated with C – H out-of-plane deformation modes assigned at 773 and 730 cm^{-1} are supposed to undergo slight positive shift due to tightening of the aromatic ring on complexation[19]. A positive shift of *ca.* 10 cm^{-1} has been observed in this mode of vibration which is in conformity with the observations of earlier workers[17-19]. The characteristic, Zr = O stretching frequency has been observed as a weak band in all the complexes at *ca.* 960 cm^{-1} [10,21].

In the region 400-350 cm^{-1}, there is a characteristic medium or weak band in the complexes. Where the ligand itself has no absorption. These new bands in this region are tentatively assigned[6,10,21] as γ(M – O) frequencies.

The presence of numerous bands in the spectra of picO complexes of ZrO(IV) complicates the identification of the nature of coordination of the

perchlorate, nitrate and thiocynate groups. However, a close comparison of the spectra makes some inference possible.

In $ZrO(picO)_4(ClO_4)_2$, the very strong ν_3 band and a strong ν_4 band are assigned to the bands observed at *ca.* 1085 and *ca.* 625 cm^{-1}, respectively, for the perchlorate ion, indicating that Td symmetry has not been disturbed and the perchlorate ions are not bonded to the zirconium ion[8,10,21].

The absence on the ν_2 band of ionic nitrate(D_{3h}) around *ca.* 1360 cm^{-1} and the occurrence of two strong bands at *ca.* 1520 and 1280 cm^{-1} in spectra of nitrato complex suggest the coordination of nitrate in these complexes[22,23]. Conclusive decision between mono and bidentate nature of nitrato groups is rather difficult. However, by applying Lever separation method[24], the two combination $(\nu_1+\nu_4)$ bands appear at 1760 and 1700 cm^{-1}. The separation is 60 cm^{-1} which suggest the bidentate nature of the nitrato groups in this complex. The bidentate nature of nitrato groups further supported by the presence of bands at *ca.* 1020 cm$^{-1}(\nu_2)$, *ca.* 800 cm$^{-1}(\nu_6)$ and *ca.* 730 cm$^{-1}(\nu_3/\nu_5)$[25].

In the thiocynato complex, $ZrO(picO)_2(NCS)_2$, the C=N stretching vibration is observed at *ca.* 2040 cm^{-1}. This may be taken as an evidence for the bending of the thiocynate through nitrogen in the ZrO(IV) complex[26]. The ν(CS) and δ(NCS) frequencies observed at 780 cm^{-1} and 480 cm^{-1} respectively further support the N-bonding to zirconium ion.

Thermal Behaviour :

The thermal investigations of zirconium(IV) complexes of amine N-oxides have been investigated to only a limited extent[7-9]. The d.t.a. of the complexes studied in reveal no peak around 100° indicating the non-hygroscopic nature of the complexes. The chloro, bromo and nitrato complexes decompose endothermically while thiocynato and perchlorato complexes decompose exothermically, the later decomposing bioleutly due to the oxygen content of the perchlorate. On decomposition, all the complexes produce carbon and metal. The small exo-peak around 400° is due to oxidation of carbon, while a final sharp exo-peak around 550° is due to complete metal oxidation.

The thermogravimetric analysis of the complexes also show the similar thermal behaviour. No change occurs upto 150°. The weight loss values observed in the thermal decomposition of oxozirconium(IV) complexes of picO correspond very closely with the following schemes :

$$ZrOCl_2.2picO \xrightarrow[(-picO)]{190^\circ} ZrOCl_2.picO \xrightarrow[(-picO)]{270^\circ} ZrOCl_2 \xrightarrow[[O]]{590^\circ} ZrO_2.$$

$$ZrOBr_2.2picO \xrightarrow[(-picO)]{170^\circ} ZrOBr_2picO \xrightarrow[(-picO)]{255^\circ} ZrOBr_2 \xrightarrow[[O]]{510^\circ} ZrO_2.$$

$$ZrONO_3.2picO \xrightarrow[(-picO)]{210^\circ} ZrO(NO_3)_2picO \xrightarrow[(-picO)]{280^\circ} ZrO(NO_3)_2 \xrightarrow[[O]]{550^\circ} ZrO_2.$$

$$ZrO(NCS)_2.2picO \xrightarrow[(-picO)]{160^\circ} ZrO(NCS)_2picO \xrightarrow[(-picO)]{230^\circ} ZrO(NCS)_2 \xrightarrow[[O]]{510^\circ} ZrO_2.$$

$$ZrO(ClO_4)_2.6picO \xrightarrow[(-2picO)]{280^\circ} ZrO(ClO_4)_2.4picO \xrightarrow[(-4picO)]{300^\circ} ZrO(ClO_4)_2 \xrightarrow[[O]]{520^\circ} ZrO_2.$$

If the minimum t.g.a. decomposition temperature is taken as a rough criterion of the thermal stability then the order for oxozirconium(IV) complexes with picO is $ClO_4 < NO_3 < Cl < Br < NCS$.

Acknowledgement

Thanks are due to U. G. C., New Delhi, and State C. S. I. R., Lucknow, for financial support.

References

1. G. GARVEY, J. H. NELSON and R. O. RAGSDALE, *Coord. Chem. Rev.*, 1968, **3**, 375.
2. N. M. KARAYANNIS, *Coord. Chem. Rev.*, 1973, **11**, 93.
3. N. M. KARAYANNIS, A. N. SPECA, D. E. CHASAN and L. L. PYTLEVESKI, *Coord. Chem. Rev.*, 1976, **20**, 37.
4. W. BYERS, A. B. P. LEVER and R. V. PARISH, *Inorg. Chem.*, 1968, **7**, 1835.
5. J. H. NELSON and R. O. RAGSDALE, *Inorg. Chim. Acta*, 1968, **2**, 439.
6. N. M. KARAYANNIS, A. N. SPECA, L. L. PYTLEVESKI and M. M. LABES, *J Less-Common Metals*, 1970, **22**, 117.
7. R. K. AGARWAL—"Studies on Complexing Behaviour of Oxygen Donor Molecules towards Th(IV) and Zr(IV)", Ph.D. Thesis, 1979, Meerut University, Meerut, (India).
8. P. RAMAMURTHY and C. C. PATEL, *Can. J. Chem.*, 1964, **42**, 856.
9. V. KRISHNAN and C. C. PATEL, *Can. J. Chem.*, 1966, **44**, 972.
10. S. K. MADAN and A. M. DONOHUE, *J. Inorg. Nuclear Chem.*, 1966, **28**, 1303.
11. A. K. MAZUMDAR and R. G. BHATTACHARYA, *Science and Culture*, 1969, **35**, 271.
12. A. K. MAZUMDAR and R. G. BHATTACHARYA, *J. Inorg. Nuclear Chem.*, 1973, **35**, 4296.
13. R. C. PAUL, S. L. CHADHA and S. K. VASHISHAT, *J. Less Common Metals*, 1968, **16**, 288.
14. P. RAMAMURTHY and C. C. PATEL, *Naturwissenschaften*, 1961, **22**, 693.
15. E. KURZ, G. KOBER and M. BERL, *Anal. Chem.*, 1958, **30**, 1983

16. Y. Kakiuti, S. Kida and J. V. Quagliano, *Spectrochim. Acta*, 1963, 19, 201.

17. N. M. Karayannis, C. M. Mikulski, M. J. Strocko, L. L. Pytlewski and M. M. Labes, *J. Inorg. Nuclear Chem.*, 1971, 33, 3185.

18. N. M. Karayannis, C. M. Mikulski, L. L. Pytlewski and M. M. Labes, *Inorg. Chem.*, 1974, 13, 1146.

19. T. N. Srivastava, P. C. Srivastava and Neelu Bhakru, *J. Indian Chem. Soc.*, 1978, 55, 484.

20. J. V. Quagliano, J. Fwjita, G. Frawz, D. J. Phillips, J. A. Walmslay and S. Y. Tyree, *J. Amer. Chem. Soc.*, 1961, 83, 3770.

21. R. K. Agarwal, A. K. Srivastava and T. N. Srivastava, *Indian J. Chem.* (In press).

22. C. C. Addison and N. Logan, *Adv. Inorg. Chem. and Radiochem.*, 1964, 6, 95.

23. N. M. Karayannis, C. M. Mikulski, L. L. Pytlewski and M. M. Labes, *J. Inorg. Nuclear Chem.*, 1972, 34, 3139.

24. A. B. P. Lever, E. Mantiovani and B. S. Ramaswamy, *Can. J. Chem.*, 1971, 49, 1957.

25. R. W. Hester and W. L. Crossman, *Inorg. Chem.*, 1966, 5, 1308.

26. J. L. Burmeister, *Coord. Chem. Rev.* 1966, 1, 205 ; 1968, 3, 225.

J. Indian Chem. Soc.,
Vol. LVII, April 1980, pp. 378-381

Preparation and Characterization of *Bis*-Dithiocarbamato Complexes of *Bis*-Biphenyl Tin(IV)

K. CHANDRA, A. K. GARG and M. C. JAIN

Department of Chemistry, S. D. College, Muzaffar Nagar, (U.P.), India

and

N. KUMAR and B. S. GARG*

Department of Chemistry, University of Delhi, Delhi-7, India

Manuscript received 2 November 1979, accepted 20 December 1979

Bis-dithiocarbamato complexes of bis-p-biphenyl tin(IV) of the type $(C_6H_5-C_6H_4)_2$-$Sn(S_2CNRR')_2$, (where R=Me, Et or i-pr; R'=$-CH_2C_6H_5$; NRR'=piperidine, 4-methylpiperidine, morpholine, 2:6 dimethylmorpholine or N-methylpiperizine), have been prepared by the reaction of appropriate anhydrous sodium salt of dithiocarbamic acid with $(C_6H_5-C_6H_4)_2SnCl_2$ in acetone. The complexes have been characterized by elemental analysis, i.r. and ^{1}H n.m.r. spectroscopy. Molecular weight determination in C_6H_6 and conductivity measurement in $PhNO_2$ indicated these complexes to be monomeric and non-electrolytic. On the basis of i.r. spectra bidentate mode of bonding between tin and dithiocarbamate ligand has been suggested.

SINCE the first report on phenyl tin dithiocarbamates[1] in 1965, a considerable number of dithiocarbamato complexes of alkyl or aryl tin(IV) have been prepared by various methods[1,2,3]. The bidentate behaviour of dithiocarbamate ligand in $R_2Sn(IV)$ and RSn(IV)N,N-disubstituted dithiocarbamato complexes is well established[1,4-7]. Complexes of the type $R_2Sn(R'_2DTC)_2$ (where R=alkyl or halogen) show i.r. spectra and dipole moment consistent with a cis arrangement of the R groups. The Mössbauer of a number of complexes were examined and on the basis of quadruple splitting (1.7 mm sec^{-1}), a *cis*-octahedral structure was postulated for bi-phenyl tin(IV) *bis*-dithiocarbamates. On the basis of larger splittings a lower coordination number for the tin atom was suggested for the analogous dialkyl complexes. The structure of the $R_2SnS_2CNR'_2$ complexes is rather uncertain, since no conclusive evidence has been advanced for either a penta or tetra coordinated tin atom in these species[8]. However, in a recent communication an unsymmetric (an isobidentate) bonding of dithiocarbamate moiety has been suggested in some $Ph_2SnS_2CNR_2$ complexes[9] on the basis of ^{1}H n.m.r. studies.

The present communication deals with the preparation and characterization of some new *bis-p*-biphenyl tin(IV) *bis*-dithiocarbamato complexes of the type $(C_6H_5-C_6H_4)_2Sn(S_2CNRR')_2$ where (R=Me, Et or i-pr and R'=$-CH_2C_6H_5$; or NRR'=piperidine, 4-methylpiperidine, morpholine, 2:6 dimethyl morpholine or N-methylpiperizine). Their i.r. and ^{1}H n.m.r. studies suggest the bidentate mode of bonding between tin and dithiocarbamato group.

Experimental

Reagents and Techniques :

Well dried and purified solvents such as C_6H_6, CH_2Cl_2, acetone, petroleum ether were used. All other chemicals used were of A.R. quality. For conductivity measurements $PhNO_2$ was purified as described by Fay and Lowry[10].

$(C_6H_5-C_6H_4)_2SnCl_2$ was prepared by the reaction of $(C_6H_5-C_6H_4)_4Sn$ and $SnCl_4$ in 1 : 1 molar ratio in a sealed tube[11,12]. $(C_6H_5-C_6H_4)_4Sn$ was prepared from p-$BrC_6H_4-C_6H_5$, $SnCl_4$ and Na in benzene by Wurtz reaction. $SnCl_4$ used was prepared by the action of pure and dry Cl_2 gas on tin metal.

The sodium salts of N-substituted dithiocarbamic acid[13] were prepared by the reaction of appropriate amine, CS_2 and NaOH in aqueous medium at 10°. These sodium salts were dried *in vacuo* first at room temperature and then at 110°, till rendered anhydrous (i.r. spectrum).

A. *Preparation of $(p$-$C_6H_5-C_6H_4)_2$-$Sn(S_2CNMeBz)_2$:*

(0.4957 g, 1 m mol) $(C_6H_5-C_6H_4)_2SnCl_2$ and (0.438 g, 2 m mol) $NaS_2CNMeBz$ were refluxed in acetone (50 cm^3) for 30 min. NaCl formed during the reaction was filtered off after cooling the reaction mixture to room temperature. The filtrate was concentrated to 10 cm^3 *in vacuo* and petroleum ether (60-80) was added dropwise with constant

TABLE 1—ELEMENTAL ANALYSES, MOLECULAR WEIGHT AND CONDUCTIVITY DATA FOR *Bis*(BIPHENYL)-TIN-*Bis*-DITHIOCARBAMATO COMPLEXES

Complex	Conductivity ohm^{-1}cm^{2}mole^{-1}	Molarity $\times 10^{-3}$	Found (Calcd)% C	H	N	Sn	M.W. Found (Calcd)	M.P.	Colour
1. $(C_6H_5-C_6H_4)_2Sn-(S_2CNMeBz)_2$	0.29	5	62.2 (61.7)	4.9 (4.65)	3.12 (3.43)	13.9 (14.68)	831 (817)	105°	Faint yellow
2. $(C_6H_5-C_6H_4)_2Sn-(S_2CNEtBz)_2$	0.30	5	62.9 (62.48)	5.4 (4.97)	2.8 (3.31)	13.4 (14.20)	856 (845)	108°	Faint yellow
3. $(C_6H_5-C_6H_4)_2Sn-(S_2CNi-PrBz)_2$	0.28	4	64.1 (63.3)	5.9 (5.34)	3.8 (3.21)	13.15 (13.63)	878 (873)	115°	Faint yellow
4. $(C_6H_5-C_6H_4)_2Sn-(S_2C\ Pipd)_2$	0.31	5	56.8 (56.64)	5.5 (5.10)	3.12 (3.76)	16.8 (15.97)	852 (745)	100°	Yellowish white
5. $(C_6H_5-C_6H_4)_2Sn-(S_2C\ 4\text{-}Me\ Pipd)_2$	0.32	6	59.68 (59.12)	5.1 (5.48)	3.32 (3.62)	15.1 (15.39)	885 (773)	105°	Yellowish white
6. $(C_6H_5-C_6H_4)_2Sn-(S_2C\ Me\ Pipz)_2$	0.25	3	56.9 (55.74)	5.8 (5.16)	6.6 (7.24)	15.96 (15.48)	761 (775)	210°	White
7. $(C_6H_5-C_6H_4)_2Sn-(S_2C\ Mor)_2$	0.28	5	53.7 (53.14)	4.08 (4.54)	3.21 (3.74)	15.2 (15.89)	760 (749)	110°	Whitish
8. $(C_6H_5-C_6H_4)_2Sn-(S_2C\ 2,6\ diMe\ Mor)_2$	0.28	4	56.03 (56.64)	5.67 (5.22)	2.6 (3.48)	13.9 (14.78)	793 (805)	115°	Whitish

shaking to ensure the complete precipitation. A yellowish white precipitate was collected on a G4 sintered glass frit and dried *in vacuo*. The residue on recrystallization from a 1 : 1 mixture of CH_2Cl_2 and petroleum ether (40-60°) gave a faint yellow crystalline product in $>$90% yield. Analytical and physical data are given in Table 1.

The other dithiocarbamato complexes were prepared in high yield by the same procedure as given above.

Physical Measurements :

The i.r. spectra in the region 4000-250 cm^{-1} were recorded on Perkin-Elmer Model-621 grating spectrometer using KBr pellets. ^{1}H n.m.r. spectra were recorded in $CDCl_3$ on Perkin-Elmer R-32 spectrophotometer at a sweep width of 900 Hz using TMS as internal standard. The molecular weight of the complexes were determined ebulliscopically in benzene and conductivity measurements were carried out in $PhNO_2$ using Beckman R-18 conductivity bridge.

Results and Discussion

The complexes reported herein have been prepared by the reaction of sodium salt of the respective dithiocarbamic acid on $(p\text{-}C_6H_5-C_6H_4)_2SnCl_2$ in acetone.

$$(C_6H_5-C_6H_4)_2SnCl_2+2NaS_2CNRR' \longrightarrow (C_6H_5\text{-}C_6H_4)_2Sn(S_2CNRR')_2+2NaCl$$

(where R = Me, Et or i-pr and R' = $CH_2C_6H_5$; or NRR' = piperidine, 4-methylpiperidine, morpholine, 2 : 6 dimethyl morpholine or N-methylpiperizine).

The isolated products were of good purity indicated by satisfactory results of elemental analyses (Table 1), ^{1}H n.m.r. spectroscopy (Table 3)

TABLE 2—VIBRATIONAL FREQUENCIES OBSERVED IN THE i.r. SPECTRA OF *Bis-p*-BIPHENYL TIN(IV) DITHIOCARBAMATO COMPLEXES

Complexes	Position of band (in cm^{-1}) $\nu(C-N)$	$\nu(C-S)$	$\nu(M-S)$
1. $(C_6H_5-C_6H_4)_2Sn(S_2CNMeBz)_2$	1495s	1010s	385m
2. $(C_6H_5-C_6H_4)_2Sn(S_2CNEtBz)_2$	1505s	1000s	390m
3. $(C_6H_5-C_6H_4)_2Sn(S_2CN\ i\text{-}PrBz)_2$	1495s	1005s	370m
4. $(C_6H_5-C_6H_4)_2Sn(S_2C\ Pipd)_2$	1509s	998s	378m
5. $(C_6H_5-C_6H_4)_2Sn(S_2C\ 4\text{-}Me\ Pipd)_2$	1485s	1000s	370m
6. $(C_6H_5-C_6H_4)_2Sn(S_2CMe\ Pipz)_2$	1485s	1005s	360m
7. $(C_6H_5-C_6H_4)_2Sn(S_2C\ Mor)_2$	1490s	995s	390m
8. $(C_6H_5-C_6H_4)_2Sn(S_2C\ 2,6\ diMe\ Mor)_2$	1488s	1000s	365m

and sharp melting points. These complexes are crystalline white to faint yellow in colour and are considerably stable in inert dry atmosphere, but hydrolyse very slowly in moist air. These complexes are soluble in $CHCl_3$, CCl_4, CH_2Cl_2, C_6H_6 and are insoluble in petroleum ether.

I.r. Spectra :

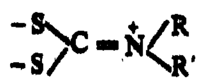
The interpretation of i.r. spectra of dithiocarbamates of transition and non-transition metals had aroused considerable interest both diagnostically as well as to assess the nature of bonding of the dithiocarbamate ligand[2,14-17]. In the i.r. spectra of these complexes, three main regions are important (i) the region 1550-1450 cm^{-1} which is associated with the thioureide band due to $\nu_{(C-N)}$ vibration of $S_2C=NRR'$ ligand, (ii) the region

TABLE 3—PROTON CHEMICAL SHIFTS (τ VALUES IN p.p.m.) IN $CDCl_3$ FOR DITHIOCARBAMATO COMPLEXES OF $(C_6H_5-C_6H_4)_2Sn(IV)$

	Complexes	Resonance due to biphenyl protons d	t	d	Resonance due to proton of groups attached to N-atom of DTC ligand
1.	$(C_6H_5-C_6H_4)_2Sn(S_2CNMeBz)_2$	2.08	2.20	2.50	4.83 (due to $-CH_2$ of $-CH_2C_6H_5$) 6.64 (due to $-CH_3$)
2.	$(C_6H_5-C_6H_4)_2Sn(S_2CNEtBz)_2$	2.39	2.60	2.72	4.95 (due to $-CH_2$ of $-CH_2C_6H_5$) 6.22 ($-CH_2$) q, 8.77 ($-CH_3$) t
3.	$(C_6H_5-C_6H_4)_2Sn(S_2CNi-PrBz)_2$	2.16	2.40	2.62	4.80 (due to $-CH_2$ of $-CH_2C_6H_5$) 6.5 ($\rightarrow$CH) m, 8.85 ($-CH_3$) d
4.	$(C_6H_5-C_6H_4)_2Sn(S_2C\ Pipd)_2$	1.94	2.36	2.60	6.08 ($-NCH_2$) 8.36 ($C-CH_2$)
5.	$(C_6H_5-C_6H_4)_2Sn(S_2C\ 4\text{-}Me\ Pipd)_2$	1.98	2.41	2.64	5.3 ($-N-CH_2$) d 6.92 ($C-CH_2$) t 8.5 ($-CH$) m 9.1 ($C-CH_3$) d
6.	$(C_6H_5-C_6H_4)_2Sn(S_2CMe\ Pipz)_2$	1.99	2.35	2.58	5.88 ($-NCH_2$) t 7.5 ($-NCH_2$) t 7.68 ($-CH_3$)
7.	$(C_6H_5-C_6H_4)_2Sn(S_2C\ Mor)_2$	1.94	2.36	2.6	6.13 ($-NCH_2$) 7.85 ($-OCH_2$)
8.	$(C_6H_5-C_6H_4)_2Sn(S_2C\ 2,6\ diMe-Mor)_2$	1.95	2.39	2.63	5.37,7.27 ($-NCH_2$) 6.3 ($-CH$) m 8.83 ($-CH_3$) d

1050-950 cm^{-1} which is associated with $\nu_{(C-S)}$ vibration and (iii) the region 400-350 cm^{-1}, associated with $\nu_{(M-S)}$ vibration.

The presence of an absorption band around 1500 cm^{-1} is accepted as arising from a polar structure as shown below :



The increasing donor character in R or R' provides the stability to this structure and increases $\nu_{(C-N)}$[17,18]. Only one band appearing in the region 1050-950 cm^{-1} was assumed by Ugo and Bonati[8] as characteristic of symmetrically bonded bidentate ligand, however, two bands indicate one uncomplexed (C=S) and one complexed (C−S) group, therefore appearance of two bands ~1000 cm^{-1} indicate the monodentate mode of binding. Brinkhoff and Gotens[19] and Colapietro *et al.*[20] have indicated that for the ligand bonded slightly unsymmetrically, two bands with the separation <20 cm^{-1} appears at ~1000 cm^{-1}. The band appearing at ~380 cm^{-1} is characteristics for $\nu_{(M-S)}$ in these complexes.

In the i.r. spectra of the complexes described in this paper (Table 2), a band appears at ~1500 cm^{-1} which is characteristic of $\nu_{(C-N)}$ of $S_2C\text{=}NRR'$ whereas another band appears at ~1000 cm^{-1} which is characteristic of $\nu_{(C=S)}$. Only one band is observed in the region ~1000 cm^{-1} indicating that in these complexes dithiocarbamate ligands are bidentate and symmetrically bonded to tin metal. Sharp band ~380 cm^{-1} is attributed to Sn−S bond in these complexes.

^{1}H n.m.r. Spectra :

The benzyl group in *bis*-p-biphenyl tin(IV) *bis*-dithiocarbamato complexes (No. 1-3, Table 3) is indicated by the presence of a singlet ~4.8 τ due to $-CH_2$ protons however signal due to phenyl protons of benzyl group get mixed with the proton signals due to biphenyl ligand. Complex No. 1 shows a sharp singlet at 6.64 τ due to $N-CH_3$ protons. Complex No. 2 shows a quaternion at 6.22 τ (CH_2 protons) and a triplet at 8.77 τ (due to $-CH_3$ protons) of the ethyl group. In complex No. 3, a multiplet at 6.5 τ and a doublet at 8.85 τ due to the $\rightarrow$CH and $-CH_3$ protons identify the i-pr group.

The piperidine group in compound no. 4 is identified with the appearance of two sharp signals ~6.08 τ (due to $-N-CH_2$ protons) and ~8.36 τ (due to $C-CH_2$ protons)[21-23]. A doublet at 5.3 τ ($N-CH_2$), a triplet at 6.92 τ ($C-CH_2$), a multiplet at 8.5 τ ($-CH$) and a doublet at 9.1 τ ($C-CH_3$) protons characterize the presence of 4-methylpiperidine group in complex No. 5. The N-methylpiperizine group in complex No. 6 shows two types of resonance signals due to $N-CH_2$ protons, i.e. a triplet at 5.88 τ due to CH_2 protons bounded to the N of the DTC group and a triplet at 7.5 τ due to CH_2 protons on the other N bonded to the CH_3 group. The CH_3 protons show a singlet at 7.68 τ[24]. The morpholine group in complex No. 7 is indicated with the presence of two types of resonance signals due to CH_2 protons, i.e. at 6.13 τ ($-N-CH_2$ protons) and 7.85 τ ($-O-CH_2$ protons)[24]. The 2,6 dimethyl morpholine group in complex No. 8 is identified with the presence of two types of resonance signals at 5.37 τ and 7.27 τ due to $N-CH_2$ protons, a complex multiplet at 6.3 τ due to CH protons and doublet at 8.83 τ due to the CH_3 protons.

The resonance due to biphenyl protons appears in the form of a doublet, a triplet and a doublet between (2−3 τ)[25,26].

The i.r. and ^1H n.m.r. studies of these complexes indicate that dithiocarbamate ligands are bidentate chelating and a coordination number of 6 may be assigned to tin atom in these complexes having an octahedral geometry. Moreover, in case of octahedral geometry two structures namely *cis* and *trans* are possible. *Cis* configuration[8] is more consistent for these complexes as the $\nu_{(C-N)}$ is towards the higher frequency (i.r. discussion).

Acknowledgement

One of the authors (K.C.) is thankful to University Grants Commission, New Delhi for the award of a teacher fellowship under the Faculty Improvement Programme.

References

1. E. J. KUPCHIK and P. J. CALABRETTA, *Inorg. Chem.*, 1965, **4**, 973.
2. F. BONATI and R. UGO, *J. Organometal Chem.*, 1967, **10**, 257.
3. K. JONES and M. F. LAPPERT, *Proc. Chem. Soc.*, 1962, 358 ; *Chem. Abs.*, 1963, **58**, 5711.
4. J. C. MAY, D. PETRIDIS and C. CURRAN, *Inorg. Chim. Acta*, 1971, **5**, 551.
5. H. HONDA, K. KOMURA, V. KAWASKI, T. TANAKA and R. OKAWARA, *J. Inorg. Nuclear Chem.*, 1968, **30**, 3231.
6. T. KIMURA, N. YASUOKA, N. KASAI and M. KAKUDO, *Bull. Chem. Soc.* Japan, 1972, **45**, 1649.
7. E. O. SCHLEMPER, Private communication.
8. B. W. FITZSIMMONS, *Chem. Comm.*, 1968, 1485.
9. R. D. JAMES, G. DOMAZETIS and B. J. MAGEE, *J. Organometal Chem.*, 1977, **57**, 141.
10. R. C. FAY and R. N. LOWRY, *Inorg. Chem.*, 1967, **6**, 1512.
11. G. BAHR and R. GELIUS, *Chem. Ber.*, 1958, **91**, 812.
12. T. V. TALALAEVA, N. A. ZAITSEVA and K. A. KOCHESHKOV, *J. Gen. Chem.* (U.S.S.R.), 1946, **16**, 901 ; *Chem. Abs.*, 1947, **41**, 2014.
13. H. L. KLOPPING and G. J. M. VANDERKERK, *Recl. Trav. Chim. Pays-Bas*, 1951, **70**, 917.
14. D. COUCOUVANIS, *Prog. Inorg. Chem.*, 1970, **11**, 233.
15. J. CHATT, L. A. DUNCANSON and L. M. VENANZI, *Nature*, 1956, **117**, 1042.
16. H. BRINKHOFF, Ph. D. THESIS, Nijmegen (1970).
17. D. C. BRADLEY and M. H. GITLITZ, *J. Chem. Soc.* (*A*), 1969, 1152.
18. F. A. COTTON and J. A. MCCLEVERTY, *Inorg. Chem.*, 1964, 3, 1398.
19. H. BRINKHOFF and A. M. GOTENS, *Rec. Trav. Chim.*, 1971, **111**, 252.
20. M. COLAPIETRO, A. VACIAGO, L. ZAMBONELLI, P. L. LOADER and L. M. VENANZI, *Chem. Comm.*, 1966, 476.
21. E. LIPPERT and H. PRIGGE, *Ber, Bunsenges, Physik Chem.*, 1963, 67, 415.
22. J. B. LAMBERT and R. G. KESKE, *J. Amer. Chem. Soc.*, 1966, **88**, 620.
23. H. WEITKAMP and F. KORTE, *Chem. Ber.*, 1962, **95**, 2896.
24. N. S. BHACCA, L. F. JOHNSON and J. N. SCHOOLERY (Vol. 1), N. S. BHACCA, D. P. HOLLIS, L. F. JOHNSON and E. A. PIER (Vol. II), N. M. R. spectra catalog, Vols. I and II, Varian Associates 1962 and 1963.
25. F. A. BOVEY, F. P. HOOD, E. PIER and H. E. WEAVER, *J. Amer. Chem. Soc.*, 1965, **87**, 2058.
26. R. E. MAYO and J. H. GOLDSTEIN, *Molecular Physics*, 1965, **10**, 301.

J. Indian Chem. Soc.,
Vol. LVII, April 1980, pp. 382-384

Electrode Kinetics and Formation Constants of Mixed Complexes

K. D. GUPTA, K. K. CHOUDHARY and J. N. GAUR

Chemistry Department, University of Rajasthan, Jaipur-302 004

Manuscript received 10 May 1977, revised 24 February 1978, accepted 3 March 1978

Attempts have been made for the determination of kinetic parameters of mixed system of zinc with 1 : 2 propane diamine and 1 : 3 propane diamine keeping the concentration of the weaker ligand 1 : 3 propane diamine constant and varying the stronger ligand 1 : 2 propane diamine. The reduction process is found to be quasi-reversible and diffusion controlled.

VARIOUS methods have been developed to determine kinetic parameters. The first theoretical treatment of polarographic current voltage curves was attempted by Heyrovsky and Ilkovic[1]. Later the various methods developed to determine K_s (rate constant) and α are due to Neiman[2], Koutecky[3], Delahy[4], Kivolo and Oldham[5], Tamamushi and Tanaka[6], Tachi[7], Matsuda[8], Randles[9], Stromberg[10] and Sathyanarayana[11] etc.

Attempts have been made by a number of workers[12-13], for the determination of kinetic parameters in case of simple system of zinc with formate, citrate, acetate, tartrate but no attempt has been made so far in the determination of kinetic parameters for mixed complexes of zinc.

Therefore, we have made an attempt for the first time for the determination of kinetic parameters of mixed system of zinc with 1 : 2 propanediamine and 1 : 3 propanediamine. Here in mixed system the concentration of weaker ligand (1 : 3 propanediamine) is kept constant while that of stronger 1 : 2 propanediamine varied. The overall formation constants of mixed complexes have been determined by Schaap and McMasters method[14]. The present study is in succession to the mixed complex study made by us[15-17].

Theory :

The DeFord and Hume's treatment for simple complexes developed by Schaap and McMasters for mixed complexes gives a new function $F_{oo}(X, Y)$

$$F_{oo}(X, Y) = \text{antilog}\left[\frac{.435nF}{RT} E_{\frac{1}{2}} + \log\frac{I_M}{I_c}\right]$$

where various symbols have their usual significance. In Ledan's approach where the metal ion forms two complexes with ease of the ligand may be written as

$$F_{oo}(X, Y) = \beta_{oo} + \beta_{o1}[Y] + \beta_{o2}[Y]^2 + \beta_{1o} + \beta_{11}[Y, X] + \beta_{2o}[X]^2$$

or

$$F_{oo}(X, Y) = A + B[X] + C[X]^2$$

where $A = \beta_{oo} + \beta_{o1}[Y] + \beta_{o2}[Y]^2$

$B = \beta_{1o} + \beta_{11}[Y]$

and $C = \beta_{2o}$

In practice the concentration of weak ligand is maintained constant while that of stronger is varied, the original graphical method may be extended to F_{oo} data. The intercept on F_{oo} axis gives the value of A so that

$$F_{1o} = \frac{F_{oo} - A}{[X]} = B + C[X]$$

a similar plotting F_{1o} vs X and taking the intercept on F_{1o} axis as B

$$F_{2o} = \frac{F_{1o} - B}{[X]} = C$$

From the knowledge of B we can compute the value of β_{11} (mixed complex formation constant).

Experimental

Reagent grade chemicals were used during all the experimental procedure. Solution of Zn^{2+} was prepared by weighing zinc nitrate and standardised as usual. Solutions of 1 : 2 propanediamine and 1 : 3 propanediamine were used as complexing agent. The ionic strength was kept constant at 1.5*M* by adding requisite amount of sodium perchlorate. Titron X-100 was used as maximum suppessor.

The polarograms were taken manually in a H type cell saturated with NaCl agar-agar bridge. The dropping mercury electrode had the following characteristics : m = 2.16 mg/sec, t = 4.6 sec (in open circuit). The temperature was kept constant at

30±0.1° with the help of Haake type ultra thermostat. Purified nitrogen was used for deaeration.

Results and Discussion

Solutions containing 0.5 mMZn^{2+} and various concentrations of 1 : 2 propanediamine (.01, .02,..... .08*M*) were prepared at fixed concentration of 1 : 3 propanediamine (.02*M*). Requisite amount of sodium perchlorate was added to keep constant ionic strength (u = 1.5*M*). In each case a single well defined reduction wave appeared whose half-wave potential was found to shift towards more negative side and diffusion current decreased with increasing concentration of propylenediamine. The above results indicate mixed ligand complex formation between 1 : 3 propanediamine and 1 : 2 propanediamine with zinc.

The plots of i_d vs h(h is effective height of mercury column after applying back pressure and i_d vs C (concentration of the ligand) come to be linear confirming the system to be diffusion controlled. Further the plots of log $\frac{i}{i_d - i}$ vs E_{de} were linear with slope of the order of 37±2mV indicating the system to be quasi-reversible. Hence $-E^r_{\frac{1}{2}}$ reversible half-wave potentials were determined by Gellings[18] method which involves the plots of

$$\left[E+\frac{RT}{nF}\ n\frac{i}{i_d - i}\right] \text{ vs i at zero current value.}$$

As the electrode process is quasi-reversible, the kinetic parameters were determined by Gellings method which involve

$$\log (Z-1)=n\frac{1.13}{t}-(1-\alpha)$$

$$\text{where } Z=\text{antilog}\ \left[\frac{nF}{2.303RT}(E^r_{\frac{1}{2}}-E)-\log\left(\frac{i}{i_d - i}\right)\right]$$

$$\text{and } \xi=\frac{nF}{RT}\left(E-E^r_{\frac{1}{2}}\right)$$

from the slope and intercept of the log (Z−1) against $\left(E-E^r_{\frac{1}{2}}\right)$. The values of α and or K_s determined and the results have been summarised in Table 1.

The value of K_s was found to be of the order of 10^{-4} cm/sec, which confirms that the reduction process is quasi-reversible and from the table it is clear that irreversibility is increased in the presence of ligand 1 : 3 propanediamine in comparison to that of simple zinc ($K_s \times 10^3 = 4.42$ cm/sec).

In case of mixed system the values of K_s was found to be of the same order but decrease at varying concentration of the stronger ligand (1 : 2 propanediamine) showing that stronger ligand favours reversibility. The values are shown in Table 1.

TABLE 1

Kinetic Parameters for Zn^{++} 1 : 3 Propanediamine System

C_x (moles)	$D^{\frac{1}{2}} \times 10^4$ (cm²/sec)	λ	$K_s \times 10^4$ (cm/sec)
0.01	3.3	0.3549	1.17
0.02	7.6	0.7764	2.19
0.03	9.59	0.9590	2.5
Kinetic Parameters for mixed complex Zn 1 : 2 Propanediamine-1 : 3 Propanediamine System; 1 : 3 Propanediamine = .02m fixed.			
0.01	2.5	0.9335	2.5
0.05	2.45	2.042	5.0
0.07	2.54	3.715	9.4

Simple Complexes :

The reduction of Zn^{2+} in the medium of 1 : 2 propanediamine 1 : 3 propanediamine separately was found irreversible and diffusion controlled slope as evident from the constant value $i_d/h^{\frac{1}{2}}_{eff}$. Convention logarithmic plots yield good straight lines but the resulting slopes were found not to be in agreement with theoretical values for reversible process thus indicating irreversible nature of the reduction process.

Overall formation of the simple complexes were determined by DeFord and Hume's[19] method using the polarographic measurement. The results are summarised below :

Simple species	Overall formation constant
[Zn (1 : 3 propanediamine)]$^{2+}$ log β_{01}	12.6990
[Zn (1 : 3 propanediamine)]$^{2+}$ log β_{02}	14.00
[Zn (1 : 2 propanediamine)]$^{2+}$ log β_{10}	12.6021
[Zn (1 : 2 propanediamine)$_2$]$^{2+}$ log β_{20}	15.00

Mixed Complex :

The nature of reduction of Zn^{++} in the mixed medium was the same as in individual media. The Schaap and McMasters function F_{00} was calculated over the given range of variable concentration of 1 : 2 propanediamine at one fixed concentration of 1 : 3 propanediamine.

F_{00} function and other function values along with the polarographic measurement were recorded in Table 2 at 30°. The values of B.C. as a result of graphical extrapolation are also mentioned in the table. The value of A calculated in theory.

TABLE 2—POLAROGRAPHIC MEASUREMENTS AND F_{ij} FUNCTIONS OF Zn(II) 1 : 2 PROPANEDIAMINE-1 : 3 PROPANEDIAMINE SYSTEM AT 30°C
[1 : 3 PROPANEDIAMINE] = 0.02*M* FIXED
i_d OF SIMPLE METAL ION = 90 div.
$-E_{\frac{1}{2}}$ OF SIMPLE METAL ION = 0.9810 VOLTS

C_x (in moles)	$-E_{\frac{1}{2}}$ V vs S.C.E.	i_d (div)	$F_{00}\times10^{-11}$	$F_{10}\times10^{-12}$	$F_{20}\times10^{-15}$
0.00	0.9840	90	—	—	—
0.01	1.3405	86	7.9	60.0	—
0.02	1.3555	85	25.59	12.0	2.75
0.03	1.3650	84	58.67	17.3	3.61
0.04	1.3700	81	79.75	19.5	3.25
0.05	1.3750	80	119.80	23.6	3.42
0.06	1.3805	79	180.70	29.8	3.88
0.07	1.3820	78	205.20	29.1	3.22
0.08	1.3850	79	265.00	33.0	3.31

$A = 1.4\times10^{11}$, $B = 60\times10^{12}$, $C = 3.5\times10^{15}$, $\beta_{11} = 3.0\times10^{15}$

Using the value of B at .02*M* fixed, concentration of 1 : 3 propanediamine, the value of β_{11} is calculated by the equation

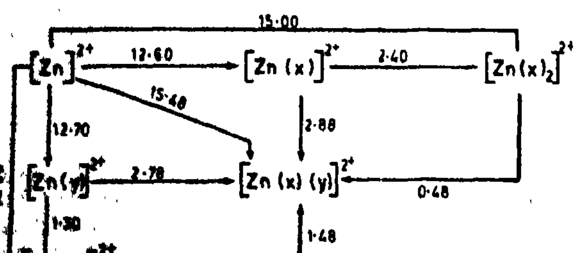
$$B = \beta_{10} + \beta_{11}(Y)$$

Discussion

The structures of 1 : 2 propanediamine and 1 : 3 propanediamine respectively are

```
CH3 - CH - CH2          CH2 - NH2
      |    |            |
     NH2 — NH2          CH2
                        |
                        CH2 - NH2
```

From the structures it is seen that 1 : 2 propanediamine is a stronger ligand than 1 : 3 propanediamine, which is also observed by our results of overall formation constants and supported by mixed complex formation.



Scheme

In the scheme numerical values are log K values where K is the equilibrium constant of the corresponding step. X and Y stand for 1 : 2 propanediamine and 1 : 3 propanediamine respectively.

It is seen from the scheme that $[Zn(Y)]^{2+}$ can add to X more easily than $[Zn(X)]^{2+}$ to [Y] and also that the tendency of $[Zn(Y)_2]^{2+}$ to add [X] is more than to add [Y]. In the same way all the above results show that approach of [X] to the metal ion is less hindered than the approach of Y. And also [X] forms stronger complexes than (Y) with Zn^{2+}.

Since the complexes of Zn^{++} with 1 : 2 propanediamine and 1 : 3 propanediamine are very much stable, they can effect the system wherever they are likely to be formed. Since the reduction of zinc is diffusion controlled, it can be estimated in the presence of 1 : 2 propanediamine and 1 : 3 propanediamine polarographically.

References

1. J. HEYROVSKY and D. ILKOVIC, *Collection Czech. Chem. Commun.*, 1956, **21**, 836.
2. N. N. NEIMAN, *Zh. Fiz. Khim.*, 1948, **32**, 1954.
3. J. KOUTECKY and J. CIZECH, *Collection Czech. Chem. Commun.*, 1956, **21**, 836.
4. P. DELAHY, *J. Amer. Chem. Soc.*, 1953, **75**, 1430.
5. P. KIVOLO, K. B. OLDHAM and H. A. LAITINEN, *J. Amer. Chem. Soc.*, 1953, **75**, 4142.
6. R. TAMANUSHI and N. TANAKA, *Bull. Chem. Soc. Japan*, 1949, **22**, 187, 227 and 1950, **23**, 1160.
7. I. TACHI, *Bull. Chem. Soc.*, 1955, **28**, 423.
8. H. MATSUDA and Y. AYABE, *Bull. Chem. Soc. Japan*, 1955, **23**, 423 and 1959, **36**, 1164.
9. J. E. B. RANDLES, *Cana. J. Chem.* 1959, **37**, 238.
10. A. G. STROMBERG, *Zh. Fiz. Khim.*, 1962, **36**, 2714.
11. S. SATHYANARAYANA, *J. Electroanal*, 1964, **7**, 403.
12. H. MATSUDA, *Z. Electrochem.* 1961, **65**, 489 ; 1958, **62**, 977.
13. H. MATSUDA and Y. AYABE, *Z. Electrochem.*, 1959, **63**, 1164.
14. W. B. SCHAAP and D. L. MCMASTERS, *J. Amer. Chem. Soc.*, 1961, **83**, 4699.
15. K. K. CHOUDHARY, S. C. BAGHEL and J. N. GAUR, *Bull. Chem. Soc.*, Japan, 1977, **50**, 243.
16. K. K. CHOUDHARY, S. C. BAGHEL and J. N. GAUR, *J. Inorg. Nuclear Chem.*, 1975, **37**, 2513-2516.
17. K. D. GUPTA, S. C. BAGHEL, K. K. CHOUDHURY and J. N. GAUR, *J. Indian Chem. Soc.* 1977, **54**, 833.
18. P. J. GELLINGS, *Z. Electrochem. Ber. Bunsenger Phys. Chem.*, 1962, **66**, 477, 481, 799 ; 1963, **67**, 167.
19. D. D. DEFORD and D. N. HUME, *J. Amer. Chem. Soc.*, 1951, **73**, 5321.

J. Indian Chem. Soc.,
Vol. LVII, April 1980, pp. 385-387

Thermal Analysis of Fe(II), Fe(III), Co(II), Ni(II) and Cu(II) Chelates of 2′-Hydroxy-4-Methoxy-5′-Methylchalkone Oxime

NARAYAN S. BHAVE and R. B. KHARAT

Chemistry Department, Nagpur University Campus, Nagpur-440 010

Manuscript received 27 November 1979, accepted 20 December 1979

The thermal analysis of Fe(II), Fe(III), Co(II), Ni(II) and Cu(II) chelates of 2′-hydroxy-4-methoxy-5′-methylchalkone oxime (HMMCO) was studied by TG and DTA techniques. All chelates show somewhat similar TG and DTA profiles when heated in an atmosphere of air. A sharp exothermic peak in the range 150-200° was observed preceded to endothermic peak for dehydration of metal chelate. This sharp exothermic peak may be caused due to the transition from unstable state to stable state of the chelate. Broad exothermic peak was observed above 300°, corresponding to rapid mass-loss in TG curve, which may be due to oxidation-reduction reactions. A relative thermal stability of metal chelates is reported.

VERY few systems are reported showing the relationship between thermal stability of metal chelates and structure of chelating agents[1]. Wendlandt[2-5] and Hill[6,7], studied the thermal properties of metal chelates with various chelating ligands. Seshagiri *et al*[8], Sheshadri[9] and other workers[10-13] reported the thermal stability of metal chelates of oxime. HMMCO[13] readily form chelates with transition metal ions[14]. The purpose of this study is to report thermal stability of the metal chelates. The techniques employed are thermogravimetry (TG) and differential thermal analysis (DTA).

Materials and Methods :

Preparation of Metal Chelates :

Metal chelates of HMMCO were synthesized as reported earlier[14].

Thermoanalytical Techniques :

TG and DTA studies were performed in the Chemistry Department of Indian Institute of Technology, Powai, Bombay (India). A brief account of TG and DTA apparatus is given below :

Thermogravimetric Analysis : The thermal balance consists of phosphor-broze spring ; the contraction of the spring due to mass-loss was converted into electrical signals by means of a LVDT which was then amplified and fed to the recorder.

The sample holder consisted of a light platinum basket. A vertical furnace was employed for heating the sample. The sample holder was surrounded in the constant temperature zone of the furnace. Heating rate was adjusted to 5-6°/min manually. A precalibrated chromelalumel thermocouple was placed very near to the sample holder to measure the temperature. About 40-50 mg of the sample was used for each run.

Differential Thermal Analysis : The emf of the differential thermocouple was fed to a recording potentiometer.

The following conditions were maintained in all the experiments.

(a) Reference material : Al_2O_3 (Calcinied at 1200°)

(b) Heating Rate : 7-8°/min.

(c) Sample holders : Platinum cups.

(d) Weight of the sample : Nearly 50 mg.

Results and Discussion

Mass-loss Study :

The mass-loss curves of the metal chelates are shown in Fig. 1. The thermal dissociation data, including initial decomposition temperature (Ta), inflexion point temperature (Tb) and per cent-mass-loss (%W) due to the oxidation-reduction reactions[17] are incorporated in Table 1.

Fe(II)(HMMCO)$_2$.5H$_2$O :

The mass-loss curve of Fe(II) (HMMCO)$_2$.5H$_2$O is shown as curve A in Fig. 1. It can be seen that the dehydration of the Fe(II)(HMMCO)$_2$.5H$_2$O takes place between 100° and 200° (12.50% found, 11.39% ther.) as one step process. A corresponding weight loss in this range suggests the association of five water molecules with the chelate. Above 200° the

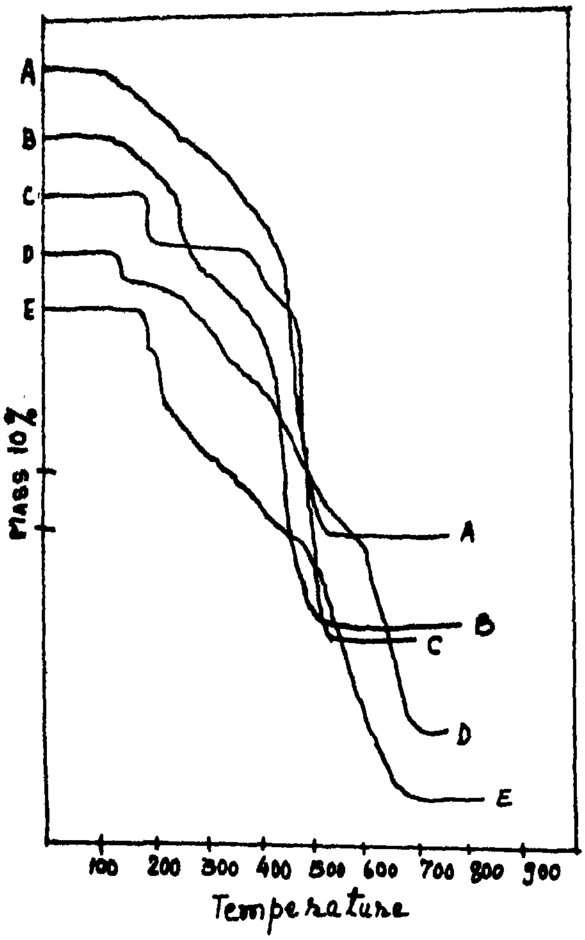


Fig. 1. TG curves, (A) Fe(II)(HMMCO)$_2$.5H_2O, (B) Fe(III)(HMMCO)$_3$.6H_2O, (C) Co(II)(HMMCO)$_2$.3H_2O, (D) Ni(II)(HMMCO)$_2$.2H_2O, (E) Cu(II)(HMMCO)$_2$.3H_2O.

TABLE 1—THERMAL STABILITY DATA OF METAL CHELATES

Chelates	Ta°(C)	Tb°(C)	%W
Fe(II)(HMMOO)$_2$.5H_2O	300	540	73
Fe(III)(HMMCO)$_3$.6H_2O	240	530	77
Co(II)(HMMCO)$_2$.3H_2O	390	540	73
Ni(II)(HMMOO)$_2$.2H_2O	260	690	80
Cu(II)(HMMCO)$_2$.3H_2O	240	680	82

Ta, Temperature of initial decomposition without considering dehydration.
Tb, Temperature at inflection point of oxidation-reduction reaction.
%W, Calculated from mass-loss curve considering only anhydrous chelate.

TG curve shows gradual mass loss upto 350° beyond which abrupt mass loss has been observed which indicates oxidation-reduction reaction[17].

Fe(III)(HMMCO)$_3$.6H_2O :

The mass-loss curve of this metal chelate is shown as curve B in Fig. 1. Fe(III)(HMMCO)$_3$.6H_2O indicates the evolution of six water molecules in temperature range 130 to 200° (11.00% found, 10.70% ther.). Further decomposition takes place above 300°.

Co(HMMCO)$_2$.3H_2O :

The mass-loss curve of this chelate is given in Fig. 1 (Curve C). Co(HMMCO)$_2$.3H_2O dehydrates between 100 and 250° (8.50% found, 7.97% ther.) and after dehydration this chelate has been observed to be stable upto 390°. Then TG curve shows rapid mass-loss which may be caused due to oxidation-reduction reactions.

Ni(HMMCO)$_2$.2H_2O :

The mass-loss curve of this chelate is shown as curve D in Fig. 1. Ni(HMMCO)$_2$.2H_2O chelate evolved 2 moles of water of hydration per mole between 100 and 180° (6.0% found, 5.46% ther.) as one step process and further decomposition takes place above 260°. Rapid mass-loss above 260° may be caused due to the oxidation-reduction reactions.

Cu(HMMCO)$_2$.3H_2O :

The mass-loss curve of this chelate is given as curve E in Fig. 1. Cu(HMMCO)$_2$.3H_2O loses the water of hydration in the temperature range 100 to 200° and continuous mass-loss is observed upto 400°, after that rapid mass-loss is observed which can be attributed to the oxidation-reduction reactions.

In general the water of hydration may be considered either as the crystal or as co-ordination water. According to Nikolav *et al*[15] water eliminating below 150° can be considered as the crystal water and water eliminatoy above 150° may be due to its coordination to the metal ion. In the present stueies it is observed that water of hydration has been eliminated between 100 and 200° which suggests the presence of water of hydration as coordinated water as well as crystal one.

In the present studies initial decomposition temperature (Ta) and inflection temperature (Tb) have been used to determine thermal stability of metal chelates. The initial decomposition temperature (Ta) is frequently used to define the relative thermal stability of metal chelates[16]. On the basis of experimental findings in the present course of studies and observations made by earlier workers[8,9,16], the relative thermal stability for HMMCO chelates can be given as

Co(II) > Fe(II) ≃ Ni(II) > Fe(III) ≃ Cu(II)

Differential Thermal Analysis :

The DTA curves of chelates are shown in Figs. 2 and 3. Small exothermic peak is observed in most of the cases below 100°, with no TG mass-loss ;

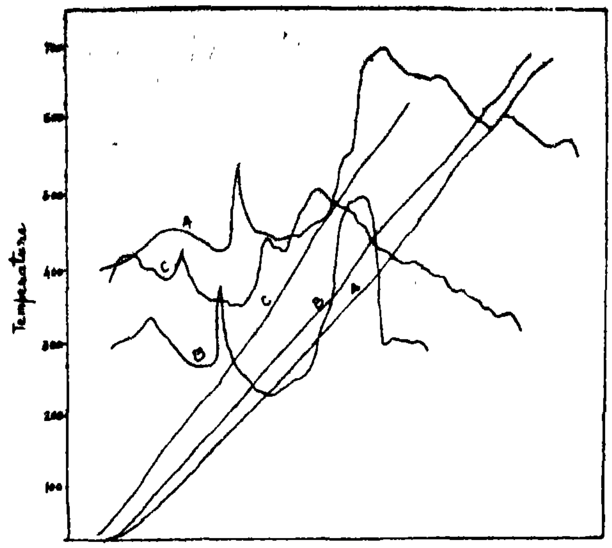


Fig. 2. DTA curves : (A) Fe(II)(HMMCO)$_2$.5H$_2$O, (B) Fe(III)(HMMCO)$_2$.6H$_2$O, (C) Co(II)(HMMCO)$_2$.5H$_2$O.

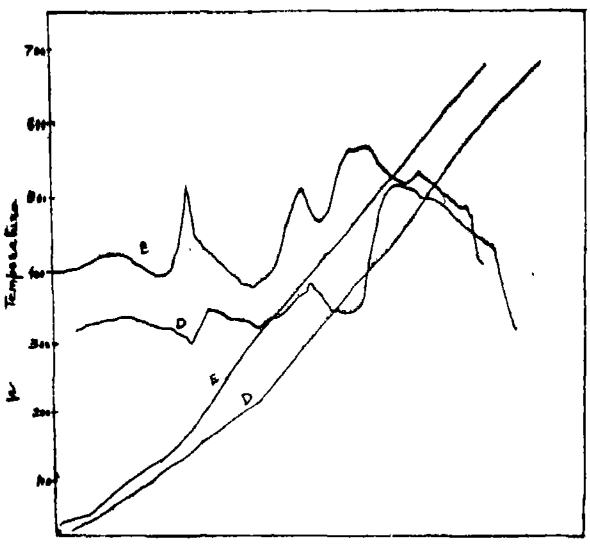


Fig. 3. DTA curves : (D) Ni(II)(HMMCO)$_2$.2H$_2$O, (E) Cu(II)(HMMCO)$_2$.3H$_2$O.

this can be interpretated in terms of isomerisation process[16]. Endothermic and exothermic peaks of DTA curves for almost all chelates in the temperature range 150-230° indicate dehydration and transition of unstable to stable state of chelates respectively. The appearance of sharp exothermic peaks in this temperature range has been demonstrated by earlier workers[16] for the transition of one state to another. Further, all broad DTA curves are characterized by exothermic peak in the temperature range of 300 to 600° as observed in other chelates of oxime[8,9]. In all the cases, however, the exothermic peak was preceded by a broad endothermic peak. This behaviour can be interpreted in terms of the dissociation of the chelates followed by exothermic oxidation-reduction reactions. Such type of observation was noted by Chang and Wendlendt[17] earlier. It is observed that DTA peaks temperature and mass-loss temperature on TG curve do not coincide with each other. This is probably due to the fact that separate instruments have been employed for TG and DTA studies.

Acknowledgement

The authors express their gratitude to Late Prof. A. B. Biswas, I.I.T., Powai, Bombay, India, for the facilities given for thermal analysis (TG and DTA) studies. Thanks are due to Prof. K. N. Munshi, Head, Department of Chemistry, Nagpur University, Nagpur, India, for the requisite facilities.

References

1. W. W. Wendlandt, *Anal. Chim. Acta.*, 1957, **17**, 428.
2. G. D. 'Ascenzo and W. W. Wendlandt, *J. Thermal Anal.*, 1969, **1**, 423.
3. G. D. 'Ascenzo and W. W. Wendlandt, *Anal. Chim. Acta*, 1970, **50**, 79.
4. F. C. Chang and W. W. Wendlandt, *Thermochimica Acta*, 1971, **2**, 293.
5. D. L. Perry, C. Vaz and W. W. Wendlandt, *Thermochimica Acta*, 1974, **9**, 76.
6. C. G. Scency, J. O. Hill and R. J. Magee, *Thermochimica Acta*, 1975, **11**, 301.
7. C. G. Scency, J. F. Smith, J. O. Hill and R. J. Magee, *J. Thermal Anal.*, 1976, **9**, 415.
8. V. Seshagiri, S. Rao and Brahmji, *Z. Anal. Chem.*, 1972, **262**, 275.
9. R. Sheshadri Naidu and R. Raghava Naidu. *Indian J. Chem.*, 1977, **15A**, 652.
10. G. Liptay, E. Papp Molnor and K. Burger, *J. Inorg. Nuclear Chem.*, 1969, **31**, 247.
11. R. S. Bottei and D. L. Greene, *J. Inorg. Nuclear Chem.*, 1968, **30**, 1469.
12. R. S. Bottei and C. P. McEachern, *J. Inorg. Nuclear Chem.*, 1970, **32**, 2653.
13. B. K. Deshmukh, C. N. Vyas and R. B. Kharat, *J. Indian Chem. Soc.*, 1978, **32**, 389.
14. Narayan S. Bhave and R. B. Kharat, *J. Indian Chem. Soc.*, 1979, **56**, 244.
15. A. V. Nikolaev, V. A. Logvinenko and L. I. Myachina, Thermal Analysis, Academic Press, New York, 1969, Vol. 2, 779.
16. W. W. Wendlandt and J. P. Smith, The Thermal Properties of Transition Metal Ammine Complexes, Elsevier, Amsterdam, 1967, p. 195.
17. F. C. Chang and W. W. Wendlandt, *Thermochimica Acta*, 1973, **7**, 103.

J. Indian Chem. Soc.,
Vol. LVII, April 1980, pp. 388-390

5-Phenylazo Salicylaldehyde Complexes of Transition Metals as Potential Semiconductors

LEELA PARDESHI, A. RASHEED and RAMESH A. BHOBE*

Department of Chemistry, Marathwada University, Aurangabad-431 004

Manuscript received 7 September 1978, revised 30 November 1979, accepted 4 March 1980

The D. C. conductivities of solid metal complexes of transition metal ions Cu(II), Ni(II), Co(II), Mn(II) with phenylazo salicylaldehydes in their pellet form are reported. It is found that semiconducting behaviour is observed only when the complexes get pyrolysed in the range ~310 to 340°K.

SEMICONDUCTION of complexes of metals or compounds of metals has gained sufficient ground in recent years. Some work on the semiconducting properties of rare earth complexes of Fluorescein[1] was reported from these laboratories. Fielding[2] have investigated some complexes for their semiconducting properties and has come to the conclusion that complexes containing metal atom in different oxidation states in crystallographically equivalent positions are capable of acting as semiconductors. Infact, the experiments concluded by this worker showed $Fe_4[(Fe(CN)_6)]_3$ as an intrinsic semiconductor. Ksendzov and Strongova[3] have shown an interconnection of electrical conductivity with exchange interaction of ions and electrons in 3d shells. Even in compounds of the type $CoFe_2O_4$, semiconducting properties have been discovered[4]. Unusual high value of conduction, explained on quantum mechanical tunnel model, was proposed by Kwan and Zwickel[5] in the case of tris(*o*-phenanthroline) Fe(II) hexachloro-iridate and its analogs withdipyridyl. Intrinsic semiconduction was observed by some workers[6] in the case of transition metal complexes of 6-mercaptopurine and 4-mercapto-6, 7-diphenylpteridine. Since delocalised electrons and conjugation impart semiconducting properties to compounds, the present worker thought that the metal complexes of *p*-phenylazo salicylaldehydes, having azo-dye as one of the constituents, may well serve as potential semiconductors.

Experimental

The complexes were prepared as reported earlier[7-9]. The D.C. conductivity of the complexes were determined in their pellet form using Elico Million Megohmmeter model R.M. 70 R. The instrument could read and measure upto 10^{14} ohms and the test voltage varied from 100 to 500 volts; the accuracy being at the lower range ±5%. The pellet of the test sample was put in a typical cell fabricated in this laboratory and resistance in Megohms was calculated using the expression.

Resistance in Megohms = Meter reading × Applied voltage × Multiplying factor.

Multiplying factor being 10, 10^2, 10^3, etc., in the present investigation.

The sample was heated in a tubular furnace in which D. C. conductivity cell snugly fitted, the temperature of the furnace being increased by steps from room temperature to about 200° and regulated by using Dimmerstat and Sunvic dial.

The slope values obtained from log ρ vs 1/T were converted to Ea values in eV by using expression :

$$\text{Slope } (-\text{ve}) = Ea/2.303 \times 0.864 \times 10^{-4}$$

It is to be noted that resistivities (σ) of these samples were obtained only after subjecting them to several tem erature increase, temperature-drop cycles.

During the D. C. conductivity measurements several errors crop in. Grain boundaries are developed during compression, metallic particles of the die may get adhered to during pelletisation or there may be an imperfect contact of the electrodes to the pellet due to slight deformation during pellet formation. The present worker applied several compression cycles before taking the final results of the conductivity measurements and only limiting values were chosen as standard. The metallic particles, possibly adhered to the pellet, were gently removed by scrapping the pellet with stainless steel blade so as to not disturb the physical dimensions of it. The pellet was smeared with silver paint to ensure a good contact with the electrodes. Care was also taken not to apply very high voltages to avoid any leakages across the border. Results of D. C. conductivities given in Table 1 are only for those samples which gave satisfactory reproducibility.

* Senior author for correspondence.

TABLE 1—SOME TYPICAL VALUES OF log σ FOR THE 5-PHENYLAZO SALICYLALDEHYDE COMPLEXES OF TRANSITION METALS. FIRST COLUMN UNDER THE COMPLEX GIVES TEMPERATURE (°K) AND THE SECOND ONE log $\sigma - \overline{12}$ AND THOSE MARKED WITH ASTERISK log $\sigma - \overline{9}$

Mn(II)-*o*-TAS		Ni(II)-*m*-TAS	
312.5	1.54	315.45	1.72
416.6	2.10	431.03	2.10
Mn(II)-*m*-Cl-PAS		Ni(II)-*p*-TAS	
312.5	0.98	299.40	2.40
416.6	1.18	384.61	2.48
Mn(II)-*p*-TAS		Ni(II)-*o*-Cl-PAS	
303.03	1.34	317.46	1.00
416 06	1.60	432.90	1.28
Mn(II)-*p*-Cl-PAS		Ni(II)-*m*-Cl-PAS	
312.5	1.09	283.28	1.58
416.6	1.60	322.58	2.60
Mn(II)-*m*-TAS		Ni(II)-*p*-Cl-PAS	
312.5	0.28	285.70	2.28
434.78	0.38	322.58	2.60
Co(II)-*p*-TAS		Cu(II)-*m*-TAS	
294.11	1.22	333.33	0 80*
341.29	1.12	400.00	0.88*
Co(II)-*o*-Cl-PAS		Cu(II)-*o*-TAS	
303.03	0.80	291.54	1.20*
411.52	1.60	416.66	0.76*
Co(II)-PAS		Cu(II)-PAS	
312.50	1.09	312.50	1.46*
416.66	1.52	400.00	2.20*
Co(II)-*m*-Cl-PAS			
322.50	1.46		
416.66	1.56		
Co(II)-*o*-TAS			
317.46	0.46		
413.22	0.58		
Cu(II)-*p*-Cl-PAS			
303.03	1.59		
370.30	1.98		
Cu(II)-*p*-TAS			
341.29	0.80		
431.03	0.92		

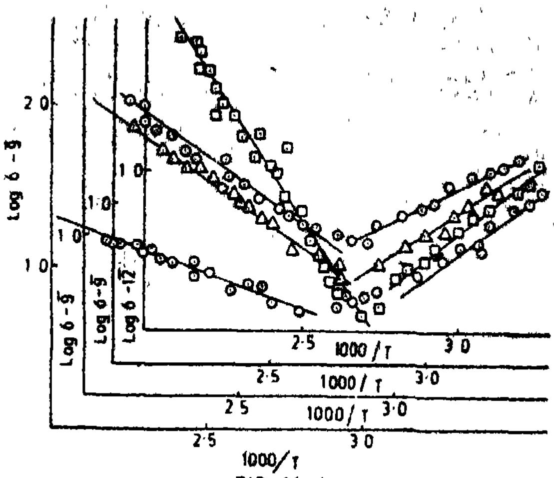


FIG 1(a)

○ Cu(II)-Complex of *o*-Tas
△ Cu(II)-Complex of *m*-Tas
⊙ Cu(II) Complex of *p*-Tas
▣ Cu(II) Complex of Pas

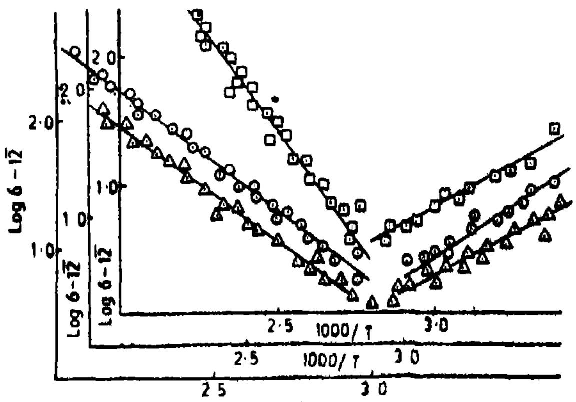


FIG 1(b)

○ Cu(II) Complex of *o*-Chloropas
△ Cu(II) Complex of *m*-Chloropas
▣ Cu(II) Complex of *p*-Chloropas

Results and Discussion

The resistance vaules of the pellets of the salts ranging from ~room temperature (27°) to 180° were converted into conductivity values (σ) by taking into account the thickness of the pellet and its diameter and evaluating thickness/area parameter of the pellet of a particular salt. Generally the diameter of the pellet remained constant (~1.307 cm) since the same die was used and the thickness varied from 0.228 to 0.287 cm according to the amount of sample pressed. The results of the D. C. conductivities are presented here in the form of plots of log 6-12 vs 1000/T as the range of conductivities was found to be $10\text{-}10^{12}$ to $10^{14}\Omega^{-1}$ cm^{-1}. It will be seen from the plots (Figs. 1a and 1b), where for the sake of brevity only one typical plot (Fig. 1a, b for Cu(II) salts has been given) that there is a consistent fall of conductivity as the temperature rises roughly from room temperature ~300°K to ~350°K and later on there is a rise in conductivity with a rise of temperature showing a definite semiconduction.

The initial trend is a typical of metallic conduction[4] where conductivity (σ) decreases as temperature rises while the latter part of behaviour is a characteristic of semiconduction. Bhobe and his collaborator[1,7-9] have found that the typical values of Ea from the relation $\log \zeta = \log \zeta_0 + Ea/kT$ ranging from 0.2 to 0.7 eV fall in the category of semiconduction. It was also observed that there was no change in the composition of the complex in the range of ~300°K to 350°K and C, H, N and M analyses of the samples kept at 300°, 363° and 480°K shows little variation (C±0.18%, H±0.3%, N±0.5%), but the substance got an internal conversion due to pyrolysis though not positively suggested by the analyses. The products were analysed at each stage of the temperature and the composition was found to be intact. The initial analysis (300°K) of the complexes when they were subjected to resistance measurements are summarised as :

The C, H, N and M analyses of the complexes as found are Cu(II)-PAS 62.20, 4.00, 10.24, 12.44 ; -*o*-Cl-PAS, 54.40 3.21, 10.26, 10.84 ; -*m*-Cl-PAS,

53.45, 2.25. 9.68; 10.00, -*p*-Cl-PAS 52.85, 2.88, 10.00, 10.79; -*o*-TAS, 58.29, 5.28, 10.42, 10.79; -*p*-TAS 63.00, 4.50, 10.82, 11.42; Ni(II) -*o*-Cl-PAS 50.58, 3.22, 9.10, 10.20; -*m*-Cl-PAS 54.56, 3.10, 9.55, 9.78; -*p*-Cl-PAS 51.10, 3.20, 9.30, 9.53; -*m*-TAS 62.40, 4.00, 10.40, 11.07; *p*-TAS 58.42, 4.50, 9.77, 10.37; Co(II)-PAS 58.40, 5.00, 10.02, 58.02; -*o*-Cl-PAS 51.18, 3.40, 9.64, 9.48; -*m*-Cl-PAS 51.05, 4.18, 9.52, 9.35; *o*-TAS 58.40, 5.00, 9.80, 10.63; -*p*-TAS 58.74, 4.81, 9.65, 10.00; Mn(II) -*m*-Cl-PAS 52.60, 4.26, -, 9.50; -*p*-Cl-PAS 51.78, 3.65, -, 9.44; *o*-TAS 62.45, 4.50, -, 9.35; -*m*-TAS 60.18, 4.18, -, 9.45; -*p*-TAS 60.20, 4.60, -, 10.25. These analyses agree very well with those calculated.

TABLE 2—ENERGY GAP VALUES (= Ea) OF COMPLEXES OF 5-PHENYLAZO SALICYLALDEHYDES

Complexes	Ea, eV
Cu(II) :	
PAS	0.765
o-chloro-PAS	0.303
m-chloro-PAS	0.436
p-chloro-PAS	0.088
o-TAS	0.153
m-TAS	0.327, 0.547
p-TAS	0.114
Ni(II) :	
o-chloro-PAS	0.452, 0.818
m-chloro-PAS	0.227
p-chloro-PAS	0.781
m-TAS	0.887
p-TAS	0.182, 0.179
Co(II) :	
PAS	0.332
o-chloro-PAS	0.901
m-chloro-PAS	0.398
o-TAS	0.153
p-TAS	0.746
Mn(II) :	
m-chloro-PAS	0.159
p-chloro-PAS	0.211
o-TAS	0.162
m-TAS	0.318
p-TAS	0.265

PAS = Phenylazo salicylaldehyde.
TAS = Toluene azo salicylaldehyde.

It will be observed from the Ea values given in Table 2, that these values generally increase in the complexes of chloro substituted PAS from ortho to para as Ea (*o*-Cl-PAS), Ea (*m*-Cl-PAS) < Ea (*p*-Cl-PAS). This case seems to be favourable for delocalised electrons. In general, chlorosubstituted complexes show greater Ea values than methyl substituted ones.

The nature of conduction (*n* or *p* type) in the complexes investigated could not be established because of lack of instrumentation for measuring Hall-Coefficients and the difficulty in getting the complexes as well-defined crystals.

Acknowledgement

The authors (Leela Pardeshi and A. Rasheed), thank the Professor and Head of the Department, Dr. K. A. Thakar for extending them the facilities for conducting post-doctoral work.

References

1. R. A. BHOBE, *J. Indian Chem. Soc.*, 1974, **51**, 846.
2. P. E. FIELDING, *J. Chem. Phys.*, 1954, **22**, 1153.
3. YA. M. KSENDZOV and V. A. STRONGOVA, *Proc. Intern. Conf. Semicond. Phys.*, Prague, 1960, **92.**
4. G. H. JONKER, *Phys.* and *Chem. Solids*, 1959, **9**, 165.
5. S. C. KWAN and A. M. ZWICKEL, *U. S. Dept. Comm. Office Tech. Service A. D.* 1963, **7**, 296; 1965, **62**, 7706.
6. S. CHATTERJEE, A. K. GHOSE and ABROHOMSOHIS, *J. Indian Chem. Soc.*, 1967, **44**, 183.
7. K. G. DESHMUKH and R. A. BHOBE, *J. Indian Chem. Soc.*, 1977, **54**, 975.
8. K G. DESHMUKH and R. A. BHOBE, *J. Inorg. Nuclear Chem.*, 1978, **49**, 135.
9. K. G. DESHMUKH and R. A. BHOBE, *Curr. Sci.*, 1977, **46**, 67.

J. Indian Chem. Soc.,
Vol LVII, April 1980, pp. 391-394

Ion Exchange Properties of Zirconium Molybdate and Zirconium Tungstate—I

R. K. SRIVASTAVA, B. PAL and B. B. RAIZADA

Department of Chemistry, D. B. S. College, Dehradun

and

K. B. PANDEYA

Department of Chemistry, University of Delhi, Delhi

Manuscript received 18 September 1979, accepted 30 December 1979

Zirconium molybdate and tungstate were obtained by adding aqueous solution of zirconium oxychloride to aqueous solutions of ammonium molybdate and sodium tungstate. pH-metric studies reveal that both the materials exhibit ion exchange properties. The thermogravimetric analysis of the samples indicate that both the exchanger materials contain about 11-12% of hydrated water which is released slowly within the temperature range 90 to 240° in case of zirconium molybdate and within 80 to 180° in the case of zirconium tungstate. The sorption of ammines of Zn(II), Cu(II), Cd(II) and Ni(II) on the above exchangers have been studied at different ionic concentrations of the external solutions. In each case the sorption increases with increase in the external concentration (0.01 to 0.10*M*), attains a maximum at 0.10*M* and then decreases with further increase in the concentration. The sorption capacity, q_A, follows the order :

Zn(II)-ammine > Cu(II)-ammine > Cd(II)-ammine > Ni(II)-ammine.

A survey of the available literature[1-6] indicates an inadequate understanding of the ion exchange properties of zirconium molybdate and zirconium tungstate. A few interesting separations have been described by using these materials as ion exchangers[4-6]. This paper incorporates a more systematic study of the ion exchange properties of these materials starting from their method of preparation. The paper includes, in brief, the study of the following aspects :

(i) Preparation of the exchanger material and determination of time required for maximum exchange, i.e. the equilibration period,

(ii) Thermogravimetric analysis of the samples,

(iii) *p*H-metric studies,

(iv) Determination of the sorption capacity, q_A, using some divalent metallic ammine complexes at their varying concentrations in the external solution, and

(v) Effect of the addition of the buffering agent on the exchange capacity q_A.

Experimental

All the reagents used, unless otherwise stated, were of the C. P. Grade. All the experiments were carried out in doubly distilled water.

Preparation of the exchanger materials :

(a) *Zirconium molybdate :* Zirconium molybdate was prepared by adding slight excess of ammonium molybdate to an aqueous solution of zirconium oxychloride in basic medium (*p*H = 8.0). The precipitate thus obtained was washed free of the Cl^- ions and dried at 40°. The dried precipitate was brought to the required particle size by grinding and sieving.

(b) *Zirconium tungstate :* Zirconium tungstate was obtained by adding slight excess of sodium tungstate solution to an aqueous solution of zirconium oxychloride. The precipitate thus obtained was worked out as above.

Preparation of the stock solution of ammines : Stock solutions of ammine complexes of the metal ions Zn(II), Cu(II), Cd(II) and Ni(II) of different ionic concentrations were prepared by dissolving required quantities of their water soluble salts in aqueous ammonia (1 : 4). The *p*H of the solutions were adjusted to 10.0 by the addition of 1 : 4 ammonia solution or 0.10 *M* HCl solution.

Determination of the metal ion content : The metal ion contents of the solutions were determined by applying standard complexometric titration method[7]. Copper was determined by the standard iodometric method.

Determination of the exchange capacity q_A : A typical procedure is described below. 25 ml of the stock solution containing a test metal ion of the specified *p*H and ionic concentration was introduced into a stoppered conical flask containing 250 mg of the exchanger material and the mixture was shaken for a predetermined period (3 hours in case of zirconium molybdate and 4 hours in case of zirconium tungstate). The equilibrated supernatant liquid containing the unsorbed metal ion was separated from the solid exchanger by centrifugation and its total metallic content was determined complexometrically. Knowing the concentration of the exchanging ion initially and after equilibration, the amount exchanged in the exchanger material (q_A) was determined.

Method for pH titration : 5 gms each of the two exchangers was converted into H-form completely by repeated exchange with 1 *M* HCl solution. A procedure, in brief, is described below. The samples of the zirconium molybdate and tungstate were introduced into stoppered conical flasks and shaken with 50 ml of 1 *M* HCl for half an hour ; the sample was separated from acid by decantation and washed thrice with double-distilled water by decantation method. To this sample 50 ml of 1 *M* HCl was again added and the procedure repeated five times. The sample thus obtained was introduced into column and 100 ml of 1 *M* HCl passed through it at the rate of 1 ml/min. Finally the sample was washed thoroughly with double distilled water to remove any free acid adhered to the sample and dried at 40°.

One gram of this sample was taken in a 100 ml beaker, added with 50 ml of double distilled water and titrated against 0.20 *M* NaOH solution *p*H-metrically. NaOH was added in fractions of 0.10 ml through a micro burette and after each addition of NaOH the beaker was shaken mechanically till constant *p*H was obtained.

Results and Discussion

The results of these investigations are presented in Tables 1 and 2, the *p*H-titration curves are shown in Fig. 1. A perusal of the data reveal the following points :

1. From Fig. 1 it is seen that the volume of 0.20 *M* NaOH required to raise the *p*H of the free acid solution is much less than the amount of NaOH required to raise the *p*H of the solution containing one gram of zirconium molybdate and zirconium tungstate from *p*H 6 to 10 in each case.

TABLE 1—TIME OF SHAKING vs AMOUNT EXCHANGED ON Zr-MOLYBDATE AND Zr-TUNGSTATE
AMOUNT OF THE EXCHANGER MATERIAL=250 mg
TOTAL VOLUME=25 ml
CONCENTRATION OF THE EXTERNAL SOLUTION=0.10*M*
*p*H OF THE SOLUTION=9.5

Time of shaking (in hours)	Amount exchanged (in m. equiv.)							
	Zr-Molybdate				Zr-Tungstate			
	Zn(II)-ammine	Cu(II)-ammine	Cd(II)-ammine	Ni(II)-ammine	Zn(II)-ammine	Cu(II)-ammine	Cd(II)-ammine	Ni(II)-ammine
1.0	0.164	0.046	0.038	0.038	0.184	0.038	0.030	0.030
2.0	0.185	0.080	0.046	0.037	0.208	0.065	0.050	0.045
3.0	0.300	0.150	0.056	0.054	0.224	0.084	0.080	0.068
4.0	0.300	0.150	0.056	0.0 7	0.265	0.099	0.097	0.081
5.0	0.300	0.150	0.056	0.087	0.265	0.099	0.097	0.081

TABLE 2 - CONCENTRATION vs AMOUNT EXCHANGED ON Zr-MOLYBDATE AND Zr-TUNGSTATE
AMOUNT OF THE EXCHANGER MATERIAL=250 mg
TOTAL VOLUME=25 ml.
*p*H OF THE EQUILIBRIUM SOLUTION=9.5

Concentration (in *M*)	Amount exchanged (in m. equiv.)							
	Zr-molybdate				Zr-tungstate			
	Zn(II)-ammine	Cu(II)-ammine	Cd(II)-ammine	Ni(II)-ammine	Zn(II)-ammine	Cu(II)-ammine	Cd(II)-ammine	Ni(II)-ammine
0.01	0.163	0.037	0.034	0.033	0.148	0.060	0.048	0.040
0.02	0.168	0.060	0.038	0.033	0.200	0.067	0.052	0.040
0.05	0.220	0.067	0.048	0.037	0.224	0.075	0.057	0.054
0.075	0.240	0.1·2	0.049	0.054	0.224	0.090	0.082	0.054
0.10	0.300	0.150	0.098	0.087	0.265	0.097	0.089	0.081
0.15	0.220	0.185	0.053	0.054	0.204	0.060	0.055	0.054
0.20	0.180	0.075	0.047	0.054	0.143	0.045	0.055	0.054

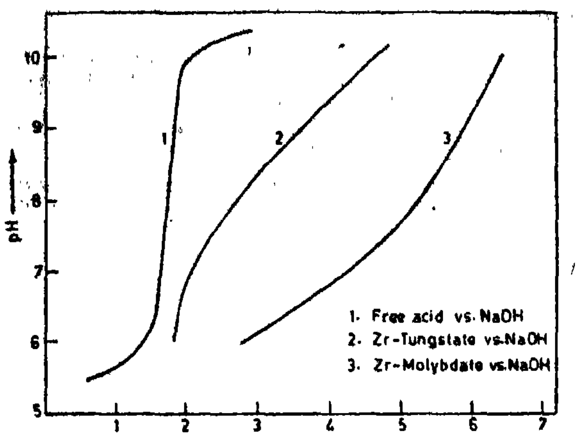


Fig. 1. pH-METRIC TITRATION CURVE

2. The thermogravimetric analysis reveals that both the exchangers contain about 11 to 12% of hydrated water which is lost slowly within the range 90 to 240° in case of zirconium molybdate and 80 to 180° in case of zirconium tungstate.

3. From Table 1 it is clear that the time required for complete sorption is 3 hours and 4 hours in case of exchange with zirconium molybdate and zirconium tungstate respectively.

4. Data in Table 2 indicate that the value of the sorption capacity, q_A, increases with increase in the external concentration, attains a maximum and then decreases with further increase in concentration.

5. The Zn(II)-ammine complex has the greatest sorption capacity (Table 2) at all concentrations in both the exchanger materials. Other ammines follow the order :

Zn(II)-ammine>Cu(II)-ammine>Cd(II)-ammine >Ni(II)-ammine.

6. The addition of the buffering agent decreases the sorption capaeity, q_A, in general.

Recently, inorganic cation exchangers with much more satisfactory properties have been prepared by combining Group IV oxides with more acidic Group V and Group VI oxides[8-10]. In case of zirconium molybdate, tungstate and phosphate the ratio of Mo/Zr, W/Zr and P/Zr has been found to be equal to 2. The meterials prepared by us have been found to be insoluble in the acidic as well as in the basic medium under which the experiments have been carried out (*p*H 1 to 12). However, they are completely soluble in highly acidic medium ($\sim 2M$ HCl). In analogy with the known structure of zirconium phosphate, probable structures to the zirconium molybdate and tungstate may be assigned as O_2MoO-Zr-$OMoO_2$ and O_2WO-Zr-OWO_2, respectively.

Analysis of the pH-titration curve (*Fig. 1*) : From *p*H-metric titrations the consumption of more amount of NaOH when the solution to be titrated contained the solid zirconium molybdate and tungstate seems to be utilized for the neutralisation of the mobile (exchangeable) H^+ ions attached to the solids. The analysis of the curve show that both the exchangers are of the weak acid type and the exchange is very slow as after each addition of the NaOH fraction (0.10 ml) the beaker had to be shaken for about half an hour to obtain constant *p*H value.

Thermogravimetric analysis : The thermogravimetric analysis of the samples indicates the presence of about 11 to 12% of the hydrated water which is lost very slowly within the temperature range 90 to 240° in case of zirconium molybdate and within the range 80 to 180° in case of zirconium tungstate. There is no evidence for the decomposition of the solids within the temperature range studied. The thermogravimetric analysis was carried out on the 'SETRAM' thermogravimetric analyser obtained from France.

Determination of the equilibration time : The time required for the maximum exchange of a particular ion has been determined by equilibrating the exchanger materials with the exchanging ions for different periods of time. Minimum time required for the maximum exchange has been taken as the equilibration time.

Effect of exchanging ion concentration : The decrease in the sorption capacity, q_A, at higher external concentrations of the exchanging ions (Table 2) is presumably due to the possible lowering of the ionic activity at higher concentrations. A diminution of the exchange potential at higher concentrations is well known[11].

Effect of the nature of the exchanging ion : Ionic potential (charge/radius), of the exchanging ion is mainly responsible for its relative exchange-rate. Since all the ions under study have identical formal charge of +2, the rate of exchange should solely depend upon the size of the complex ion. Simple ionic radii of the metal ions involved are in the order[12] : Cu^{2+}, 0.72 Å, Zn^{2+} 0.74 Å, Ni^{2+}, 0.78 Å and Cd^{2+}, 0.97 Å. But the symmetry of the various ammines has also to be considered before making an estimate about the relative sizes of these metal-ammines. $[Zn(NH_3)_4]^{2+}$ and $[Cd(NH_3)_4]^{2+}$ are tetrahedral, $[Cu(NH_3)_4]^{2+}$ is distorted square planar and $[Ni(NH_3)_6]^{2+}$ is octahedral[12,13]. Since the tetrahedral geometry involves a more compact structure than either of square-planar or octahedral geometries, the ionic sizes of these metal ammines are expected to follow

the order :

Zn(II)-ammine < Cu(II)-ammine < Cd(II)-ammine < Ni(II)-ammine.

The values of ionic potential, ϕ (charge/radius), will, therefore be in the reverse order. Observed sequence in the q_A values for different ammines follows the order of the ϕ values[14] as expected.

Effect of addition of the buffering agent : This study was carried-out to obtain the lower *p*H values in which ammine complexes remain soluble in the external solution. Normally, the complexes are decomposed at *p*H 8.0 in the absence of the buffering agent while they remain soluble when buffering agents are added even at *p*H 8.0. It has been observed that the addition of the buffering agent decreases the q_A values in all the cases which may be due to the increase in the competing NH_4^+ ions.

Acknowledgement

The authors are thankful to the U.G.C., New Delhi for financial assistance and to Dr. N. K. Kaushik, Department of Chemistry, University of Delhi, Delhi for the T. G. A. work.

References

1. K. A. KRAUS, H. O. PHILLIPS, T. A. CARLSON and J. S. JOHNSON, Proc. IInd Inter. Confer. Peaceful Uses of Atomic Energy, Geneva, 1958, **28**, 3.
2. K. A. KRAUS, T. A. CARLSON and J. S. JOHNSON, *Nature*, 1956, **177**, 128.
3. A. CLEARFIELD, Zirconium Molybdate and Tungstate Report, TAM Div. National Lead Co., Niagara Falls, N. Y., 1964.
4. M. H. CAMPBELL, *Anal. Chem.*, 1965, **37**, 252.
5. W. J. MAECK, M. E. KUSSY and J. E. REIN, *Anal. Chem.*, 1963, **35**, 2080.
6. J. M. P. CABRAL, *J. Chromatog.*, 1960, **4**, 80.
7. H. A. FLASCHKA, 'EDTA Titrations', 2nd Ed., Pergamon, Oxford, 1964.
8. C. B. AMPHLETT, Inorganic Ion Exchangers', Elsevier, Amsterdam, 1964, p. 11.
9. F. HELFFERICH, 'Ion Exchange', McGraw Hill, U.S.A. 1962, p. 14.
10. C. B. AMPHLETT, L. A. MCDONALD and M. J. REDMAN, *Chem. and Ind.*, 1956, 1314.
11. R. KUNIN, 'Elements of Ion Exchange', Reinhold, N. Y., 1960, p. 13.
12. C. K. JORGENSON, 'Inorganic Complexes', Academic Press, London, 1963, Chapt. 4.
13. F. A. COTTON and G. WILKINSON, 'Advanced Inorganic Chemistry', Wiley Eastern Pvt. Ltd., New Delhi, 1970.
14. G. H. CARTLEDGE, *J. Amer. Chem. Soc.*, 1928, **50**, 2855.

J. Indian Chem. Soc.,
Vol. LVII, April 1980, pp. 395-397

Studies on an Electrochemical Cell : Cu/CuCl/Pt

MAHENDRA PRASAD* and J. K. SRIVASTAVA

Department of Physical Chemistry, National Sugar Institute, Kanpur, India

Manuscript received 8 January 1979, revised 22 October 1979, accepted 4 March 1980

An electrochemical cell made up of CuCl pellet with copper and platinum disc electrodes has been studied. The maximum current available is about 800 μA in presence of a few milli moles of water. The charge transport in CuCl through positive holes diffusion due to concentration gradient has been suggested which is favoured by the solution of a quadratic equation of positive holes diffusion.

THE assembly of cuprous chloride pellet having the electrode configuration : Cu/CuCl/Pt was first used by Wagner and Wagner[1] for estimating the fraction of positive hole conductivity in CuCl in the temperature range of 250° to 400°. The working principle of the electrode configuration as envisaged by Wagner *et al* was, that after applying a positive E.M.F. to the Pt electrode (applied potential less than decomposition potential of CuCl) all interstitials, cuprous ions would be diffused from Pt side of pellet towards the copper electrode and under steady state condition when all Cu^+ are exhausted the current is exclusively carried by positive holes. Harrison and Prasad[2,3] later used this electrode configuration for the determination of electronic-ionic transition in CuCl in the temperature range of 24° to 240° where some part of the results below 130° were ambiguous. While attempting to observe this ambiguity, Prasad and Srivastava[4] (this work) observed that at room temperature even without applying any E.M.F. this electrode assembly produces current of the order of microamps and this current increase many fold in presence of moisture as described here.

Experimental

Cuprous chloride (A.R., B.D.H.) was dissolved in 6*M* HCl and CuCl was precipitated in distilled water. White precipitate of CuCl was washed with acetone and absolute alcohol. Solid mass was filtered, dried in vacuum and stored in vacuum desiccator for further use. Pellets were prepared from 1.5 gm of material at a pressure of 750 lbs for three minutes in a Punch and Die model 341-20 (N. J., U.S.A.). The diameter of pellet was 13 mm and thickness was 2 mm. Pellet was sandwiched between a bright weighed copper and Pt disc electrodes. The contact was ensured by an external spring. Low short circuit current of the cell was measured with the help of a microammeter model No. 474 (KYCEE) and the higher current with the help of an ammeter model 301 Weston. The E.M.F. of the cell was measured with the help of Avometer TFMI (APLAB) and H. P. Electrometer and AC resistance at 10 0 cps with Beckman Conductivity meter model RC-18 A.

Results and Discussion

First of all the measurements were made in absence of moisture and thereafter the cell was brought in contact with miosture. Pellet of CuCl sandwiched between copper and platinum disc electrodes acts itself as a cell with copper as a negative and platinum as a positive electrode, giving a current of the order of a microamps. Though the short circuit current was measured the results have been described in terms of current density. The current density in absence of moisture was ~1.0 $\mu A\ cm^{-2}$ which remained constant for hours. Some variable E.M.F. from 0.46 volt to 0.75 volt were observed. However, most samples gave an E.M.F. of 0.75 volt and therefore this value is taken for discussion. The specific resistance of the cell was ~4.50×10^6 ohm cm. These parameters of the cell were reproducible for each cell made from different pellets within 5%.

The result in presence of moisture were drastically different. The current density begins to rise at the rate of 4.4 $\mu A\ cm^{-2}\ min^{-1}$ as soon as the moisture comes in contact with CuCl pellet. The current density, E.M.F. and resistance measured after 20 minutes of moisture absorption were found to be 90 $\mu A\ cm^{-2}$, 0.46 volt and 5×10^3 ohms cm respectively. This trend of increase of current density continued approximately for three hours giving a maximum value of 800 $\mu A\ cm^{-2}$. Under this condition the E.M.F. of the cell and resistance were found to be 0.11 volt and 950 ohms cm respectively. Further increase in the current was not observed rather this value remained stationary for three hours. The aforesaid behaviour of current and time has been shown in Fig. 1. This behaviour was found to be reasonably reproducible from cell to cell made from different pellets. Further measurements that is after six hours were terminated

* Present Address : Center for Solid State Science, Arizona State University, Tempe, Arizona 85281, U.S.A.

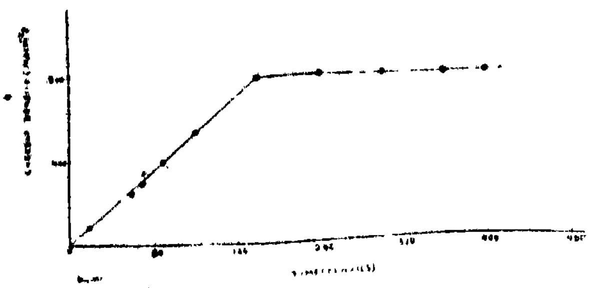


Fig. 1.

since pellet becomes relatively more moist and therefore the data up to three hours only have been taken for discussion.

The history of pellet seems to play some significant role in the system since it was observed that the E.M.F. and the resistance of the cell were not reproducible on used pellets. Other noticeable change was the adherence of cupric chloride (bluish compound) on the open surface of pellet. A film of white cuprous chloride was also observed on Pt electrode. There was a weight loss in copper electrode but only less than 0.1% of the lost copper was found to be deposited on the platinum electrode. This was determined in a separate experiment continued for three weeks.

For the interpretation of the results described above it is necessary to know what would be the driving force which could sustain the current of the cell. The data of current density and E.M.F. obtained in the absence of moisture indicate that some kind of solid state electrode reactions are taking place. It is, therefore, suggested that the probable electrode reaction could be :

Oxidation at the copper electrode	$Cu \rightarrow Cu^{+} + e$	... (1)
Reduction at the Pt electrode	$Cu^{++} + e \rightarrow Cu^{+}$	... (2)
Overall cell reaction	$Cu^{++} + Cu \rightarrow 2Cu^{+}$	... (3)

This cell reaction would correspond to a change in free energy of -74KJ which should give an E.M.F. of 0.767 volt. Such an E.M.F. across a high impedance cell ($\sim 10^{6}$ ohms) should correspond to an ohmic current of a few microamps. The observed values of E.M.F. and current density are 0.75 volt and 1.20 $\mu A\ cm^{-2}$ respectively. Such a close agreement between the expected and observed values shows that the cell appears to behave as a pseudo galvanic cell under moisture free condition with only difference that cell material as a high impedance p-type semiconductor.

Now as soon as the cell comes in contact with the moisture the situation changes. Enormous rise in the current density at the rate of 4 $\mu A\ cm^{-2}\ min^{-1}$ up to 800 $\mu A\ cm^{-2}$ and decrease of E.M.F. from 0.75 volt down to 0.11 volt clearly show that the electrode reactions referred above are greatly influenced by the presence of moisture. We believe that in presence of moisture the oxidation of cuprous chloride to cupric state is favoured as per this stoichiometry.

$$4CuCl + 2H_2O + O_2 = 2CuCl_2 + 2Cu(OH)_2 \quad \ldots (4)$$

This oxidation has two main effects from the charge transport standpoint (i) it sets free the electrons of Cu^{+} and (ii) it increases the concentration of positive holes in CuCl.

The increase in the concentration of positive holes in CuCl may be visualized from the following arguments. The valence band structure of cuprous chloride is of mixed character[5] in which the contribution of wave function of Cu-3d orbitals and Cl-3p orbitals are about 80% and 20% respectively. Foreign anions absorbed by CuCl combines with the electrons of Cu-3d making Cu^{+} as if Cu^{++} exists in CuCl lattice (Zn S). This deficiency of Cu-3d electrons caused by foreign anions amounts a positive hole in the valence band and it would behave as a positive charge carrier as long as Cu^{++} remains a part of CuCl.

If this is true then as a result of this oxidation of CuCl by moisture, eventually all Cu^{+} after becoming Cu^{++} should tend to form its own lattice. But since copper is in contact with CuCl pellet, this tendency of Cu^{++} would be minimised. In other words, deficiency of Cu^{+} in CuCl created by Cu^{++} is compensated by oxidation of Cu, i.e. $Cu \rightarrow Cu^{+} + e$. This tends to maintain CuCl close to original stoichiometry. Thus a chain type of oxidation that is $Cu \rightarrow Cu^{+} \rightarrow Cu^{++}$ sets in. The reduction of Cu^{++} to Cu^{+} as mentioned in equation (2) at the Pt electrode does not possibly compete with the oxidation at the copper electrode. Thus the net effect of oxidation of CuCl by moisture is the enormous increase electrons and positive holes over their concentration already existed in CuCl before the reaction. The approximate concentration of positive holes in CuCl at 20° before the reaction with moisture estimated from current density data is $\sim 10^{13}\ cm^{-3}$ and to satisfy the current density data in moist condition the hole concentration should be of the order of $10^{19}\ cm^{-3}$. In these approximations the mobility of positive holes has been assumed to be $\sim 0.10\ cm^{2}\ volt^{-1}\ sec^{-1}$. Thus the electrons released and accumulated at the copper electrode are pushed through the external wire whereas the building up of a large concentration gradient of positive holes in CuCl perhaps acts as a driving force for transporting the positive charge through CuCl pellet and this flow of electrons and holes through external wire and pellet respectively appears to be probable cause to sustain the short circuit current in the cell.

The argument of electronic current due to concentration gradient of positive holes is further supported by the following mathematical deduction.

The diffusion of positive holes due to the concentration gradient may be written in this form[6]

$$J = -D\left(\frac{dh}{dx}\right) - \mu h\left(\frac{dE}{dx}\right) \qquad \ldots (1)$$

where J = positive hole current, D, μ, h and dh/dx and dE/dx are diuffusion coefficient, mobility, concentration, concentration gradient of positive holes and electric potential gradient respectively. Substituting the values of these parameters that is

$$D = (kT/e)\mu \text{ and } De\ dE/dx = -\mu\frac{kT}{\sigma}\frac{dh}{dx}$$

in equataion (1)

(where σ is the positive hole conductivity) the above equation can be transformed into quadratic form of μ that is

$$\left(\frac{hkT}{\sigma}\frac{dh}{dx}\right)\mu^2 - \left(\frac{kT}{e}\frac{dh}{dx}\right)\mu - J = 0 \qquad \ldots (2)$$

This equation is based on the assumption that positive hole current supersedes the ionic current and the net current results from the accumulation and diffusion of positive holes in CuCl. The solution of equation (2) is

$$\mu = \frac{\left(\frac{kT}{e}\frac{dh}{dx} \pm\right)\left\{\left(\frac{kT}{e}\frac{dh}{dx}\right)^2 + \frac{4hkT}{\sigma}\frac{dh}{dx}J\right\}^{\frac{1}{2}}}{\frac{2hkT}{\sigma}\frac{dh}{dx}} \qquad \ldots (3)$$

$$\text{or} \quad \mu = \frac{\frac{1kT}{e}\frac{dh}{dx} \pm \left(\frac{kT}{e}\frac{dh}{dx}\right)\left\{1 + \left(\frac{4hkT}{\sigma}\frac{dh}{dx}J\right/\left(\frac{kT}{e}\frac{dh}{dx}\right)^2\right\}^{\frac{1}{2}}}{\frac{2hkT}{\sigma}\frac{dh}{dx}} \qquad \ldots (4)$$

$$\text{or} \quad \mu = \frac{1}{\frac{2hkT}{\sigma}\frac{dh}{dx}}\ \frac{kT}{e}\frac{dh}{dx} \pm \frac{kT}{e}\frac{dh}{dx}\left\{1 + \frac{4hJe^2}{\sigma kT\frac{dh}{dx}}\right\}^{\frac{1}{2}} \qquad \ldots (5)$$

Expanding the terms under square root of equation (5) and after neglecting the smaller terms it becomes

$$\mu = \left\{\frac{kT}{e}\frac{dk}{dx} \pm \frac{kT}{e}\frac{dh}{dx}\left(1 + \frac{2hJe^2}{\sigma kT\frac{dh}{dx}}\right)\right\}$$

$$\left(\frac{2hkT}{\sigma}\frac{dh}{dx}\right)^{-1} \qquad \ldots (6)$$

$$\text{or} \quad \mu = \frac{\sigma}{he} + \frac{Je}{kT\ dh/dx} \qquad \ldots (7)$$

Substituting the value of $\sigma = eh\mu$ in equation (7) one can write

$$\mu = \mu + \frac{Je}{kT\ dh/dx} \qquad (8)$$

$$\text{or} \quad \frac{Je}{kT}\left(\frac{dh}{dx}\right)^{-1} = 0 \qquad \ldots (9)$$

Equation (9) predicts that $\frac{dh^{-1}}{dx} \equiv 0$ since e, kT are constants and J is the experimentally observed quantity. Thus some finite current will be observed *only if a large concentration gradient exist in the* system.

Acknowledgement

We are thankful to Dr. N. A. Ramaiah, Director, National Sugar Institute, Kanpur and Dr. S. K. D. Agarwal, Head of Physical Chemistry Division, National Sugar Institute for their interests in the work.

References

1. J. B. WAGNER and C. WAGNER, *J. Chem. Phys.* 1957, **26**, 1597.
2. L. G. HARRISON and MAHENDRA PRASAD, 56th Chemical Conference of Chemical Institute of Canada, Montreal, 1973, paper No. 242.
3. L. G. HARRISON and MAHENDRA PRASAD, *J. C. S. Faraday Trans.* I, 1974, **70**, 471.
4. MAHENDRA PRASAD and J. K. SRIVASTAVA, Annual Convention of Chemists, Indian Chemical Society, 1977, Phy-48.
5. E. CALABRESE, Ph.D. Thesis, Lehigh University, 1971.
6. N. B. NANNAY, "Solid State Chemistry", Prentice Hall, The New Jersey, 1967, p. 162.

J. Indian Chem. Soc.,
Vol. LVII, April 1980, pp. 398-401

An Equation for the Activity Coefficient of the Ions of Strong Electrolytes for Concentrations up to 0.1 N

B. N. GHOSH*

University College of Science, 92, Acharya Prafulla Chandra Road, Calcutta-700 009

Manuscript received 6 November 1979, accepted 18 March 1980

It has been shown that the Debye Hückel equation for the activity coefficient of the ions of strong electrolytes requires modification. The modification consists in replacing $(\Sigma n)^{\frac{1}{2}}$ in the expression for Kappa by $(\Sigma n)^{\frac{1}{2}}/(2\pi a)^{\frac{1}{2}}$ where $a=[(a_+)(a_-)]^{\frac{1}{2}}$, a_+ and a_- representing the "effective diameter" of the positive and negative ions of a symmetrical electrolyte and Σn the sum of the number of positive and negative ions per cc of the solution. The volume of the composite cell in the phase space containing a pair of oppositely charged ions has been defined. The modified equation has been subjected to test using the data available in the literature on HCl, NaCl, KCl and $CuSO_4$ and $ZnSO_4$ and has been found satisfactory.

TAKING into consideration interionic attraction and applying Boltzmann distribution formula and Poisson's equation, Debye and Hückel[1,2], deduced the following equations for the activity coefficient of the ions of a strong electrolyte in solution

$$-\log f_i = \frac{Ne^2 Z_i^2}{2.303(2DRT)}\left[\chi\right] \qquad (1)$$

$$-\log f_i = \frac{Ne^2 Z_i^2}{4.606(DRT)}\left[\frac{4\pi e^2 \Sigma n_i Z_i^2}{DkT}\right]^{1/2} \qquad (1a)$$

$$=0.487 Z_i^2(\mu)^{1/2} \text{ at } 0^\circ C \qquad (1b)$$

$$=0.505 Z_i^2(\mu)^{1/2} \text{ at } 25^\circ C \qquad (1c)$$

$$-\log f_i = \frac{Ne^2 Z_i^2}{4.606[DRT]}\left[\frac{\chi}{1+\chi a}\right] \qquad (2)$$

$$=\frac{Z_i^2 A(\mu)^{1/2}}{1+aB(\mu)^{1/2}} \qquad (2a)$$

The equations† (1) and (1a) have been deduced on the assumption that ions can be treated as point charges. In equation† (2) the finite size of the ions has been taken into consideration and 'a', denotes the average "effective diameter" of the ions and A and B are constants which can be calculated from theory.

Hückel[3] has proposed further modification of equation (2) by taking into consideration the effect of the electric field of an ion on the orientation of the solvent molecules around it and has deduced the following equation :

$$-\log f_i = \frac{Z_i^2 A(\mu)^{1/2}}{1+aB(\mu)^{1/2}} - c\mu \qquad (3)$$

The aforesaid equations give f_i the activity coefficient, of a particular ion. For the mean activity coefficient f of an electrolyte dissociating into ν_+ and ν_- ions having valencies Z_+ and Z_- the following expression should be used.

$$-\log f = \frac{\nu_+(Z_+)^2+\nu_-(Z_-)^2}{(\nu_++\nu_-)}\left[\frac{Ne^2}{4.606(DRT)}\right]\frac{\chi}{1+\chi a} \qquad (4)$$

The equations have been subjected to test by many investigators[4,5] and deviation from equation (1a) has been noticed for uni-univalent electrolytes such as NaCl at concentrations about 0.0005 M and above it. Deviations from equation ( ) or (2a) have also been noticed for bi-bivalent electrolytes such as $ZnSO_4$ at fairly low concentrations. Such deviations have been attributed by some authors to the neglect of terms beyond the first two in the expansion of the series

$$\exp(Z_i e\psi/kT) - \exp(-Z_i e\psi/kT)$$

for the evaluation of the charge density near the central ion. Grownwall, La Mer and Sandved[6] have used the expansion of the series up to the 5th or 6th term and also carried out approximate integration of the Poisson equation in the form of a power series. Their equation for the activity coefficient, of a symmetrical electrolyte such as

$ZnSO_4$ may be written as follows

$$-\ln f = \frac{NZ^2e^2}{2DRT}\left[\frac{\chi}{1+\chi a}\right] - \sum_{m=1}^{\infty}\left[\frac{NZ^2e^2}{DRTA}\right]^{2m+1}\left[\frac{1}{2}X_{2m+1}(\chi a) - 2mY_{2m+1}(\chi a)\right] \qquad (5)$$

† Significance of the symbols used : N—Avogadro number, e—elementary charge, Z—Valency, D—dielectric constant, R—the gas constant, T—the absolute temperature, k—the Boltzmann constant, χ=Kappa, μ—the ionic strength and m—molality.

* Present address : 30 Regent Estate, Calcutta-700 032.

Where $X(\chi a)$ and $Y(\chi a)$ are known functions of (χa) which have been evaluted and recorded in tables.

Gronwall, La Mer equation (5) is definitely better than equation (2a) of Debye and Hückel since, for an electrolyte like $ZnSO_4$, it requires a constant value of the "ionic diameter" a, to give values of $-\log f$ which agree with the observed ones up to the concentration 0.01*M*, while equation (2a) requires impossible negative values of a. This will be evident from the data recorded in page 67, Table 2.6 of L. I. Antropov's "Theoretical Electrochemistry", 1972 (English translation).

Improvement of the Debye Hückel theory adopting a different mode of approach, has been attempted by Dutta and Bagchi[7] and by Eigen and Wicke[8]. They have tried to replace Boltzmann's formula for the distribution of ions in the ion atmosphere by a new distribution formula developed by them.

Besides, those mentioned above, the following way of modifying Debye-Hückal theory may also be considered. Boltzmann's distribution law is meant for a perfect gas in which the activity coefficient of the molecules is unity. In applying it to ions in solution their activity coefficient 'f' should be taken into consideration and for an uni-univalent electrolyte the equations should be written as follows :

$$(n_+)f\,dv = n_0 f_0 \exp(-e\psi/kT)\,dv \quad \ldots \quad (6)$$

$$(n_-)f\,dv = n_0 f_0 \exp(e\psi/kT)\,dv \quad \ldots \quad (6a)$$

In the equations (6) and (6a) $(n_+)f$ and $(n_-)f$ represent the activity, per unit volume of the positive and negative ions in the volume element dv close to the central positive ion where the potential due to it is ψ and $n_0 f_0$ represents the activity of the positive and negative ions in a unit volume of the solution where ψ is zero. Therefore, the expression for χ should contain f_0/f and should be written as follows :

$$\chi = \left[\frac{4\pi e^2 \Sigma n'}{DkT} f_0/f\right]^{1/2} \quad \ldots \quad (6b)$$

According to Donnan's theory of membrane equilibria we may write :—

$(n_0 f_0)^2 = (n_+)(n_-)f^2$ or $(f_0/f)^2 = (n_+)(n_-)/n_0^2 = [n'/n_0]^2$ or $(f_0/f) = (n'/n_0)$ where $[(n_+)(n_-)]$ has been put equal to $(n')^2$.

It is to be noted that n' is greater than n_0 and the higher the value of ψ, the greater is the ratio n'/n_0. It may be looked upon as the ratio of the negative charge density in the neighbourhood of the central positive ion to that in the bulk phase where $\psi = 0$, and it may be large in a dilute solution.

In the case of colloidal electrolytes[9] somewhat similar ratio has been found to be quite large. In a palmitic acid sol the ratio $(a)_\infty/(H)_\sigma$, denoted by $-(Pa)_\infty + (PH)_\sigma = 10^{1.3} = 20$, where $(Pa)_\infty$ and $(PH)_\sigma$ represent PH close to the surface of the colloidal particle and that of the bulk phase at colloid concentration C = 40, respectively and in a clay acid sol the ratio [denoted by $-(PH)_\infty + (PH)_o$], i.e. $\left[\frac{(H)_\infty}{(H)_o}\right] = 10^{2.13} = 135$ nearly. Similar results have also been obtained with a gum arabic acid sol[10].

Replacing (f_0/f) by (n'/n_0) in equation (6b) and substituting it in the expression for χ in equation (1a) we get, for a uni-univalent electrolyte, the following expression :

$$-\log f = \frac{Ne^2}{2.303(2DRT)}\left[\frac{4\pi e^2 \Sigma n}{DkT}(n'/n_0)\right]^{1/2} \quad \ldots \quad (7)$$

where Σn represents the sum of n positive and n negative ions and is, therefore, equal to 2n.

Assuming uniform distribution of the ions in the solution the average distance L between their centres may be represented by the following expression :

$$L = (1/2n)^{1/3} \quad \ldots \quad (8)$$

Therefore, $(1/2n)^{1/2} = L\,(L)^{1/2}$ ... (8a)

Since L has the dimension of length so $(L)^{1/2}$ may be expressed as follows

$$(L)^{1/2} = (2\pi ax)^{1/2} \quad \ldots \quad (8b)$$

where a represents the ionic diameter and x, a dimensionless variable. Substituting the aforesaid values of L and $(L)^{1/2}$ in equation (8a) it may be written as follows :

$$(1/2n)^{1/2} = [(1/2n)^{1/3}][(2\pi\, ax)^{1/2}] \quad \ldots \quad (8c)$$

$$\text{or } (2n)^{1/2} = (2n)^{1/3}/(2\pi\, ax)^{1/2} \quad \ldots \quad (8d)$$

Replacing $(\Sigma n)^{1/2}$ in equation (6b) by $(2n)^{1/3}/(2\pi\, ax)^{1/2}$ we may write

$$\chi = \left(\frac{4\pi e^2}{DkT}\right)^{1/2}\left[(2n)^{1/3}/(2\pi a)^{1/2}\right]\left[\frac{(n'/n_0)}{(x)}\right]^{1/2} \quad \ldots \quad (9)$$

In equation (9) the ratio of $(n'/n_0)^{1/2}$ to $(x)^{1/2}$ may remain constant and close to unity* over a certain range of values of n. Therefore, in that range of values of n in which the aforesaid ratio

* This point has been considered in detail in the "discussion".

remains constant the following equation should hold good :

$$\chi=\left[\frac{4\pi e^2}{DkT}\right]^{1/3}\left[(2n)^{1/3}\Big/(2\pi a)^{1/3}\right] \qquad (9a)$$

Substituting in equation (1) the value of χ as found in equation (9a) and putting $n=NC/1000$, we get for symmetrical electrolytes the following expression :

$$-\log f=\frac{Ne^2}{4.606(DRT)}\left[\frac{Z_+^2+Z_-^2}{2}\right]^{3/2}\left[\frac{4\pi e^2}{DkT(2\pi a)}\right]^{1/2}\left[\frac{N2C}{1000}\right]^{1/3} \qquad \ldots\ (10)$$

In equation (10), C denotes the concentration of the electrolyte in gram moles per liter. Furthermore, *if the effective diameter of the positive and negative* ions are denoted by a_+ and a_- respectively then in †equation (10) $a=[(a_+)(a_-)]^{1/2}$. It is to be noted that the volume g of the composite cell containing a pair of oppositely charged ions of a symmetrical electrolyte in the phase space may be found from the following relation :

$$\left(\frac{1}{2n}\right)^{1/3}\left(\frac{1}{2n}\right)^{1/3}=\left(\frac{1}{2n}\right)^{2/3}(2\pi a)\chi=L^2(2\pi a)\chi$$
$$=L^3=g \qquad \ldots\ (10a)$$

It follows from equation (10) that a plot of $-\log f$ against $(c)^{1/3}$ should be linear since all the other terms in the equation are constants. This has actually been found to be the case up to $C=0.1N$ for the symmetrical electrolytes whose data are recorded in this paper, but the straight lines cut the $(c)^{1/3}$ axis at points slightly above zero. This means that f becomes unity when C is very small, less than 0.0001 *M* and it is in broad agreement with the accepted view.

Denoting the mean activity coefficient by f, putting $A\times10^{-8}$ cm$=a$ and B for the constant terms in equation (10), it may be written for an uni-univalent electrolyte as follows :

$$-\log f=[B/(A)^{1/3}][(C)^{1/3}-(C_0)^{1/3}] \qquad \ldots\ (11)$$
$$=[0.60/(A)^{1/3}][(C)^{1/3}-(C_0)^{1/3}] \text{ at } 0^\circ C \qquad \ldots\ (11a)$$
$$=[0.624/(A)^{1/3}][(C)^{1/3}-(C_0)^{1/3}] \text{ at } 25^\circ C \qquad \ldots\ (11b)$$

Similarly for a bi-bivalent electrolyte, taking the valency of the ions into consideration, we may write

$$-\log f=[8B/(A)^{1/3}][(C)^{1/3}-(C_0)^{1/3}] \qquad \ldots\ (12)$$

Verification of the equations :

The equations deduced above have been subjected to test using the data available in the literature[8,11]. The data based on freezing point measurements have been recorded in Table 1 and those on $ZnSO_4$ at 25° have been recorded in Table 2. In column 1 of the tables, under the head miscellaneous, are mentioned the electrolyte and the equation used and the constants in the equation, $B/(A)^{1/3}$ representing the observed slope. In column 2, C denotes the concentration of the electrolyte in moles per 1000 grams of water, obs.f and cal.f represent the observed and calculated mean activity coefficient f of the ions of the electrolyte. Up to $0.1M$ no distinction has been made between a molal and a molar solution in this paper.

TABLE 1—VARIATION OF f WITH c FROM FREEZING POINT MEASUREMENTS

Miscellaneous	2	3	4	5	6	7	8
HCl	C	0.0005	0.001	0.005	0.01	0.05	0.1
Eqn. used (11) $B/(A)^{1/3}=0.22$	Obs.f	0.981	0.970	0.940	0.916	0.840	0.809
$(A)^{1/3}=2.7$ $(C_0)^{1/3}=0.039$	Cal f	0.979	0.969	0.934	0.913	0.848	0.802
NaCl	C	0.0005	0.001	0.005	0.01	0.05	0.1
Eqn. used (11) $B/(A)^{1/3}=0.23$	Obs.f	0.972	0.963	0.928	0.906	0.834	0.792
$(A)^{1/3}=2.6$ $(C_0)^{1/3}=0.025$	Cal.f	0.972	0.961	0.926	0.904	0.834	0.792
KCl	C	0.0005	0.001	0.005	0.01	0.05	0.[illegible]
Eqn. used (11) $B/(A)^{1/3}=0.247$	Obs.f	0.970	0.961	0.926	0.903	0.821	0.?79
$(A)^{1/3}=2.4$ $(C_0)^{1/3}=0.025$	Cal.f	0.970	0.959	0.921	0.903	0.826	0.780
$CuSO_4$	C	0.0005	0.001	0.005	0.05	0.05	0.1
Eqn. used (12) $(8.0B)/(A)^{1/3}=1.93$	Obs.f	0.75	0.69	0.50	0.40	0.216	0.158
$(A)^{1/3}=2.48$ $(C_0)^{1/3}=0.017$	Cal.f	0.75	0.69	0.50	0.41	0.211	0.137

TABLE 2—VARIATION OF f WITH c AT 25°C

Miscellaneous						
$ZnSO_4$	C	0.0005	0.001	0.002	0.005	0.01
Eqn. used (12) $(8.0B)/(A)^{1/3}=2.28$	Obs.f	0.780	0.700	0.608	0.477	0.387
$(A)^{1/3}=2.19$ $(C_0)^{1/3}=0.032$	Cal.f	0.780	0.700	0.611	0.482	0.381

Discussion

It will be noticed from the data recorded in the Tables 1 and 2 that the observed values of the mean activity coefficient of the ions of the electrolytes mentioned agree satisfactorily with those calculated over the concentration range $0.0005M$ to $0.1M$ of the uni-univalent electrolytes and 0.0005 *M* to $0.05M$ of the bi-bivalent electrolytes. This shows that the equations(11) and (12) hold good over the aforesaid range of concentrations of the electrolytes investigated,

† $a=(a_++a_-)/2$ may also be used.

The data recorded in the tables show that $(A)^{\frac{1}{3}}$ of HCl is greater than that of NaCl or KCL indicating that the H^+ ions in water are hydrated and exist as H_3O^+. The value of $(A)^{\frac{1}{3}}$ of $CuSO_4$ is greater than that of $ZnSO_4$ and this is 'in agreement with the fact that the ionic radius of Cu^{+2} is greater than that of Zn^{+2}.

It may also be mentioned that J. C. Ghosh[12] in his theory of strong electrolytes proposed that $-\log \lambda$ varies as $1/(v)^{1/3}$ where λ and v represent respectively the equivalent conductivity and volume of the solution. Although his theory fell into disrepute because some of the assumptions made were self-contradictory and doubtful, yet the cube root relationship proposed by him is significant.

It has been stated earlier in this paper that $[(n'/n_0)/x]^{1/3}$ remains constant and close to unity over a certain range of values of n. This statement may be justified in the following way.

As already mentioned the volume of the composite cell containing a pair of oppositely charged ions may be found from equation (10a) written as $g = L^2(2\pi a)x = L^3$.

Therefore, the density of negative charge in this cell is equal to $e/L^2(2\pi a)x = d_1$ say. The volume $L^2(2\pi a)$ surrounding the central positive ion will very probably contain the same negative change e. However, let us assume that it contains 0.96e. Then d_2 the density of negative charge in this volume element is $0.96e/(2\pi a)L^2$. Now d_2/d_1 may be put equal to n'/n_0 and we may write

$$n'/n_0 = d_2/d_1 = 0.96x \quad \dots \quad (13)$$

Therefore, $(n'/n_0)^{1/3} = 0.98x^{1/3}$ and hence $[n'/n_0)/x]^{1/3}$ is equal to 0.98 which is very close to unity and is a constant. It is to be noted that according to equation (8b), $x = L/(2\pi a)$ and that the aforesaid relation sholud hold good so long as x is greater than or equal to unity.

Acknowledgement

In conclusion the author wishes to thank Dr. S. Aditya for helpful criticisms.

References

1. P. Debye and E. Hückel, *Physikal Z.*, 1923, **24**, 183, 334.
2. P. Debye and E. Hückel, *Rec. Trav. Chem.*, 1923, **42**, 597.
3. E. Hückel, *Physikal Z.*, 1925, **26**, 93.
4. M. Randal and A. P. Vanselow, *J. Amer. Chem. Soc.*, 1924, **46**, 2418.
5. L. I. Antropov, Theoretical Electrochemistry (English tr.), 1972, **65**, 26.
6. T. H. Gronwall, V. K. La Mer and K. Sandved, *Physikal Z.*, 1928, **29**, 358.
7. M. Dutta and S. N. Bagchi, *Indian J. Phys.*, 1950, **24**, 61.
8. M. Eigen and E. Wicke, *Naturwiss*, 1951, **38**, 453.
9. B. N. Ghosh, *J. Indian Chem. Soc.*, 1971, **48**, 186.
10. B. N. Ghosh, A. C. S. Symposium series, *Colloidal Dispersions and Micellar Behaviour*, 1975, **9**, 316.
11. S. Glasstone, Electrochemistry of Solutions, 1937, 119, table XXV.
12. J. C. Ghosh, *J. Chem. Soc.*, 1918, **113**, 449, 790.

J. Indian Chem. Soc.,
Vol. LVII, April 1980, pp. 402-403

Spectrophotometric Determination of Chromium(VI) Using Gallacetophenone Oxime

P. NAGESWARA RAO and K. ADINARAYANA REDDY*

Department of Chemistry, Regional Engineering College, Warangal-506 004

Manuscript received 18 November 1979, accepted 20 December 1979

Chromium(VI) reacts with gallacetophenone oxime in acid solution forming a brownish red colour complex. This system obeys Beer's Law in the range 2-16 ppm at 410 nm. The stoichiometry between Cr(VI) and the oxime is established as 1 : 1. The molar absorptivity and photometric sensitivity are $\epsilon = 3.6 \times 10^{3}$ lit. mole^{-1}cm^{-1} and 0.015 μg. cm^{-2} respectively. The method is sensitive, simple and rapid.

PHOTOMETRIC determination of microamounts of chromium when present alone or in presence of large amounts of metal ions such as iron and nickel is very important since the metal is present in water as pollutant and a minor constituent in industrially important alloys and other complex materials. However, very few rapid colorimetric methods making use of organic reagents are available since chromium in the oxidation state of three is an inert metal ion and in the valency state of six is a powerful oxidant in acid solutions and destroys the organic reagent. Only few colorimetric methods for the determination of Cr(VI) in acid solutions were reported. These include determinations with diphenyl carbazide[1], variamine blue[2], *o*-dianisidine[3], carmoism[4], starch iodide[5], resacetophenone oxime[6] etc.

The present reagent gallacetophenone oxime (2,3,4-trihydroxy acetophenone oxime) was used earlier for the spectrophotometric determination of iron, titanium and uranium[7] also the gravimetric determination of copper[8]. Further investigations on the analytical applicability of the reagent showed that it forms a brownish red complex with chromium(VI), in fairly acid solutions and common oxidizing agents did not interfere in the colour reaction. Hence, a detailed study of the colour reaction for the possible determination of chromium is carried out and the results are communicated here.

Experimental

Reagents :

Gallacetophenone oxime is prepared following the literature procedure[6,8] and a 0.1*M* solution of it is prepared in 50% aqueous ethanol. Chromium(VI) solution (0.1*M*) is prepared by dissolving the requisite amount of potassium dichromate (AR BDH) in doubly distilled water. All the chemicals used were of analytical reagent grade or equivalent.

Apparatus :

A Beckmann DK-2A UV-visible recording spectrophotometer, an ELICO spectrophotometer Model Cl-24 and an ELICO *p*H meter Model LI-10T for optical and *p*H measurements respectively.

Results and Discussion

The *p*H study of the system chromium(VI)-gallacetophenone oxime shows that a brownish red complex is formed within the *p*H range 1-2 at 410 nm, where chromium(VI) has a little absorbance and the reagent has almost nil absorbance. It is also observed that the colour intensity increased with increase in acidity. Hence the reaction is studied in presence of different acids and the colour intensity in phosphoric acid solution is found to be more compared to other acids and least sensitivity is observed with acetic acid solution. Hence phosphoric acid is chosen as the medium of reaction and maximum absorbance is obtained in the range 0.4*M* to 0.75*M*, so all the studies were carried in 0.5*M* phosphoric acid.

The absorbance of the complex is stable for four hours and for full colour development three fold excess of reagent is necessary and but six fold excess is found suitable for reproducible values. The molar absorptivity of the complex is $\epsilon = 3.6 \times 10^{3}$ lit. mole^{-1}. cm^{-1}.

Procedure :

To various aliquots of the metal ion solution (2-16 ppm) taken in 25 ml measuring flasks, added 6.25 ml of phosphoric acid (2*M*) and 1 ml of the oxime (0.1*M*). The contents of the flasks were made upto the mark with doubly distilled water. The absorbance of the resulting solution is measured at 410 nm against the reagent as blank.

Beer's Law range, sensitivity :

A linear plot obtained between absorbance and the amount of chromium(VI) in the range of 2-16 ppm at 410 nm. The photometric sensitivity[10] of the complex is 0.015 $\mu g\ cm^{-2}$.

Nature and Stoichiometry of Complex :

Ion exchange studies showed the complex is cationic in nature. Job's continuous variation method, mole ratio method and slope ratio methods showed 1 : 1 stoichiometry between chromium(VI) and gallacetophenone oxime.

Effect of Foreign ions :

In the determination of 12 ppm of chromium (VI), the effect of diverse ions were studied. Chloride, nitrate, fluoride, borate, tartrate, perchlorate, sulphate, Mn^{2+}, Zn^{2+}, Fe^{3+} did not interfere even upto 1200 ppm. The tolerance limits of other ions causing an error $\pm 2\%$ are given in parenthesis (in ppm) : Cu^{2+}(100) ; Co^{2+}(200) ; Cr^{3+}(500) ; Ni^{2+}(600) ; Mo^{6+}(70) ; W^{6+}(40) ; Ce^{4+}(10) ; MnO_4^-(220) ; $S_2O_8^=$(160) ; IO_3^-(250) ; IO_4^-(90) ; and however, Ti^{4+}, Zr^{4+} interfere in the colour reaction.

Though the molar absorptivity of diphenyl carbazide ($\epsilon = 4 \times 10^4$) is about eleven times greater than that of the present method ($\epsilon = 3.6 \times 10^3$), the former method suffers from the very disadvantage that the reagent is unstable and divergent opinions are available on the stability of diphenyl carbazide reagent. Urone[11] stated that its stability depends greatly on the type and purity of the solvent used and the aqueous solutions were described to be the least stable. According to Allen[12] the quality of the solid diphenyl carbazide varies with the supplier and depends upon the procedure, symmetrical and unsymmetrical diphenyl carbazides[13] are formed. On the other hand, the present reagent gallacetophenone oxime is very stable over a long period both in solid state and in solution. Further, the complex formation is instantaneous, and sufficiently stable. Unlike diphenyl carbazide method, the excess oxidants do not interfere to a sufficient amount in this method. And large amounts of permanganate were tolerated in presence of excess reagent. Since sulphate ion did not interfere when present in large amounts, this method is great advantage in the analysis of chrome ores and chromium alloys and steels since they are usually dissolved in $H_2SO_4 - H_3PO_4$ acids mixture[14]. And also the present method is more sensitive than resacetophenone oxime[6].

However, vanadium(V) interferes when the amount exceeds the amount of Cr(VI). But this interference is minimised by extraction with 8-hydroxy quinoline into chloroform at pH[4].

Acknowledgement

The authors thank Prof. S. Brahmaji Rao, Head, Dept. of Chemistry, PG Centre, Anantapur for his kind suggestions. One of the authors (P.N.R.) is grateful to CSIR, New Delhi for the award of Junior Research Fellowship.

References

1. C. L. Luke, *Anal. Chem.*, 1958, **30**, 2050.
2. Laszlo Erdey and F. Szabadvary, *Mayer Kem Folyoirat*, 1957, **63**, 153.
3. F. Buscarons and J. Artigas, *Anal. Chim. Acta*, 1957, **16**, 452.
4. N. M. Kravtsova and V. I. Petrashen, *Trudy Novocharkassk Politekh Inst.* 1958 (Pub. 1959), **72**, 3.
5. Geoffrey Halliwell, *Anal. Chem.*, 1960, **32**, 1041.
6. G. Abdul Huq and S. Brahmaji Rao, Annual Convention of Chemists, Abstracts, 1979.
7. K. Adinarayana Reddy, Ph.D. Thesis, S.V. University, Tirupati, 1973.
8. K. Adinarayana Reddy and Y. Krishna Reddy, *Proc. Ind. Acad. Sci.*, 1971, **74(A)**, 153.
9. A. H. Blatt, Organic Synthesis, John Wiley, New York, 1943, Coll. Vol. II, p. 304.
10. E. D. Sandell, Colorimetric Determination of Trace-metals, Interscience, New York, 1959.
11. P. F. Urone, *Anal. Chem.*, 1955, **27**, 1354.
12. T. L. Allen, *Anal. Chem.*, 1958, **30**, 447.
13. K. H. Slotta and K. R. Jacobi, *Z. Anal. Chem.*, 1929, **77**, 344.
14. F. D. Snell and G. T. Snell, "Colorimetric Methods of Analysis", Vol. II., 1949, D. Van. Nostrand Co. Inc, New York.

J. Indian Chem. Soc.,
Vol. LVII, April 1980, pp. 404-407

pH and Sorption of Anionic Dyes by Alumina and Their Column Chromatography. Part V

G. L. MUNDHARA, M. P. TIWARI,

Department of Chemistry, Govt. College of Science, Raipur (M.P.)

and

J. S. TIWARI*

Department of Chemistry, Govt. Girls' College, Raipur (M.P.), 492 001, India

Manuscript received 24 November 1979, accepted 22 December 1979

The adsorption-desorption behaviour of HCl-treated chromatographic alumina of varying surface *p*H (*p*H 3.5-8.6) with aq. solutions of anionic dyes, orange II(OG) and naphthol blue-black (NB), under a variety of conditions of time, temperature and concentration, has been investigated. The adsorption is found to be *p*H-dependent. The greater degree of adsorption in short time-interval (10-30 min), low values of heat of adsorption (−3 to −11 k cal/mole), and easy desorption with inorganic anions have been interpreted by ion-exchange mechanism. The two dyes have been separated on alumina column.

IN continuation of our study[1-3], two anionic dyes, orange II and naphthol blue-black, were taken-up to investigate their adsorption-desorption behaviour on alumina of *p*H 3.5-8.6. The results were used in their column chromatography. *p*H of alumina means its surface *p*H.

Experimental

Substrate :

Alumina samples of *p*H 3.5 to 8.0 were prepared by treating basic Brockmann alumina (*p*H 8.6) with varying concentrations of HCl—acid or water, as described earlier[1].

Solutes :

Orange II (C. I. No 15510) was prepared in the laboratory (sulphanilic acid→2-naphthol). Naphthol blue-black (Michrome No. 1113) was the Merck sample (Fig. 1). They were recrystallised thrice from ethanol : water (1 : 1, v/v), and dried at 80° for 24 hr. The homogeneity of the samples was tested chromatographically.

Procedure :

From the stock solution of the dyes (0.1 g/l) in water, 10-80 ml solutions were withdrawn, diluted to 100 ml, and estimated colorimetrically at 485 nm (OG) and 620 nm (NB) respectively[4]. Spekol spectrocolorimeter (Carl Zeiss, accuracy ± 0.5%) was used for the estimations. The absorbance of the dyes was not affected by change in *p*H (*p*H 3.5-8.0). However, OG changes its colour at *p*H$\geqslant$8.0 which could be restored by the addition of sodium acetate-acetic acid buffer (*p*H 4.5).

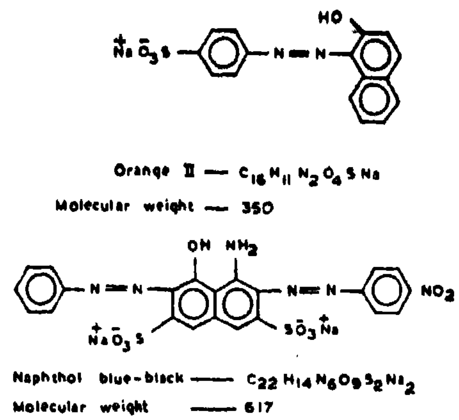


Fig. 1. Structure of orange II and Naphthol blue-black.

Adsorption experiments were conducted by equilibrating alumina (0.25 g) with the dye solutions of known concentration in 25 ml-volumetric flasks. The flasks were immersed in thermostat, and periodical shaking was made. After a specified period, 2 ml of the aliquot withdrawn, centrifuged and estimated.

* Senior Author.

Adsorption vs Time and Temperature :

The variation of adsorption as a function of time (10 min-24 hr) was studied with alumina of pH 3.5-8.0 at 30 ± 1°. The dyes show fast adsorption. Quantitative adsorption of OG occurred in 10 min (pH 3.5-5.0) and NB required 30 min for complete adsorption (pH 3.5-6.0). At higher pH, the equilibrium is almost attained in 1 hr (OG) and 4 hr (NB).

The temperature-effect studies (30°-60°) show the process to be exothermic (pH 3.5-8.0), and the isosteric heats of adsorption is calculated to be −5 to −11 k cal/mole (OG) and −3 to −5 k cal/mole (NB). Graphs and data are not shown.

Adsorption vs pH :

The results of change in the nature of adsorption with pH are shown in Figs 2 and 3. It is observed that the affinity of the solutes gradually increases with decrease in pH of the substrates. Quantitative adsorption occurs at pH 3.5-6.0 (NB) and pH 3.5-5.0(OG). The process drops to zero at pH of 8.0(OG) and 8.6 (NB). The isotherms are of L_2-type, not having a well-defined plateau, probably because of very low dye-concentrations used in the study.

Desorption Studies :

The degree of reversibility of sorption of the dyes (pH 3.5-8.0, 24 hr, 30 ±1°) was tested with a number of organic solvent-water mixtures and aq. inorganic electrolytes (*M*/100 NaCl, Na_2SO_4, Na_3PO_4) as described earlier[1].

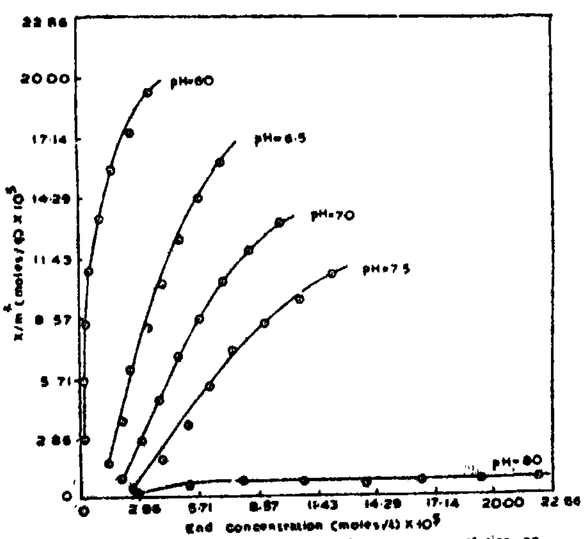


Fig. 2. Adsorption isotherms of orange II from aqueous solution on alumina of varying pH.

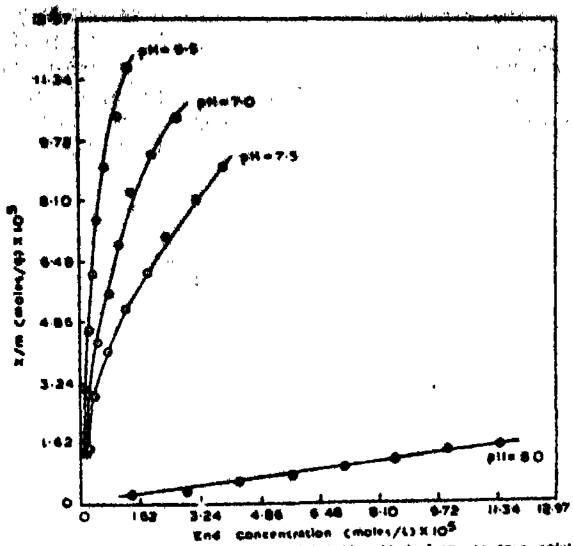


Fig. 3 Adsorption isotherms of naphthol blue-black from aqueous solution on alumina of varying pH.

The study reveals that the dyes are completely desorbed with pyridine-water (1 : 4, v/v), ethanol : *n*-butanol : buffer of the corresponding pH (1 : 1 : 2) and aq. Na_2SO_4. Sodium chloride also desorbs the dyes effectively (Table 1).

TABLE 1—DESORPTION OF OG AND NB WITH aq. NaCl

Initial concentration, 80 mg/l

Dyes	pH of alumina samples and %desorption					
pH	4.0	5.0	6.0	6.5	7.0	7.5
OG	40	60	75	90	100	100
NB	28	42	50	62	90	100

Quantitative desorption takes place with aq. Na_2SO_4 and Na_3PO_4 (*M*/100).

Results and Discussion

The dyes investigated are the sodium salts of sulphonated aromatic compounds, such as Na^+D^-. The acid-treated alumina may adsorb these anionic dyes by ion-exchange of single dye-anions or aggregated dye-anions (micelles) or through covalent bond formation with the anionic groups (e.g., sulphonate) of the dyes.

The ion-exchange is shown by :

(i) The greater degree of adsorption in a short time-interval, and low values of heat of adsorption.

(ii) *Reversibility of Adsorption :*

The desorption characteristics with inorganic electrolytes indicate ion-exchange nature of the process. The inorganic anions, it appears,

probably compete with the dye-anions at the film surface for the ionic sites. In the presence of these desorbents (1 ml, *M*/100 solution), adsorption of the dyes is retarded considerably, and in contact with PO_4^{3-} ions, it does not occur. It is likely that at low *p*H, a primary reaction of the type shown below may occur :

$$>Al^+ \vdots Cl^- + H_2PO_4^- \rightleftharpoons >Al^+ - H_2PO_4^- + Cl^-$$

Potentiometric titration results of the Cl^- ions released after adsorption of the dyes show an increase in the concentration of the ions at *p*H$\leqslant$ 6.0.

Desorption with pyridine-water is rather difficult to explain at this stage. Certain studies[6] suggest disaggregation of dyes in the presence of basic substances like pyridine, urea, dimethyl formamide, which form an adduct or complex.

(iii) pH and Adsorption :

The ionically-bound chloride content of alumina appears to decrease continuously with increasing *p*H, becoming essentially negligible in basic range. It appears that rapid exchange of the dye anions occurs at *p*H$\leqslant$5.0 (OG) and *p*H$\leqslant$6.0 (NB), followed by a slow exchange at sites within the alumina. The slow inward diffusion into the micropores of the substrates at higher *p*H may cause somewhat longer equilibrium period.

At high *p*H values, the H^+ ions of the $>Al-OH$ of the substrates tend to dissociate from the oxygen, leaving negative charge on the surface. As the *p*H is lowered, additional $-H^+$ may associate with the $-OH^-$, leaving a net positive charge, which will attract the dye-anions.

$$>Al-O...H + H^+ \rightleftharpoons >Al-OH_2^+$$

Surface at high *p*H   Surface at low *p*H

As the dye-anions are very large compared with the original ions (chloride ions), they may cover the surface with a mono-layer and screen off, to some extent, the surface forces which attracted the first layer. If screening is sufficiently good, a mono-layer will be irreversible adsorbed. This is also evident from the L_2-type of isotherms.

It is observed that NB has a greater affinity for the substrates in comparison to OG. This observation is in accordance with Roosens' suggestion[6] – greater the number of azo groups, the stronger is the adsorption. Also $-OH$ or $-NH_2$ is more effective in β-position of the naphthalene nucleus.

Thus, it appears that the adsorptive forces involved are predominantly coulombic (ion-exchange) and non-polar disperson forces. The possibility of hydrogen bonding cannot be ruled out as free $-OH$ on the dye molecules may enter into this type of bonding.

Chromatographic Separation :

Synthetic mixtures of the two dyes were separated on alumina columns. Figs 2 and 3 reveal that OG and NB show about 70% and 90% adsorption respectively on alumina of *p*H 6.5. It has also been observed that buffer of *p*H 6.5 can completely desorb both the dyes. However, the rate of migration of the two dyes in the buffer mixed with ethanol and *n*-butanol (2 : 1 : 1, v/v) is different.

Method I : Quick-fit glass column (20 × 1 cm) was packed dry with alumina (20 g) of *p*H 6.5 to a column height of 12 cm. 5.0 ml each of the two dye-solutions in water (80 mg/l) were withdrawn, mixed, applied to the column, and kept as – such for an hour. On developing the chromatogram with 10 ml of buffer of *p*H 6.5 (potassium dihydrogen-phosphate : sodium hydroxide) containing ethanol and *n*-butanol (2 : 1 : 1), two distinct bands could be seen. Upper blue band of NB (0.5 cm width), colourless space (1.5 cm) followed by orange band of OG (1 cm). OG was eluted out of the column with 30 ml of the eluent.

The NB-zone could be desorbed on elution with 20 ml of ethanol : buffer of *p*H 6.5 (1 : 4, v/v).

Method II : The dyes OG and NB show 85% and cent-per cent adsorption respectively on alumina of *p*H 6.0 (Figs 2 and 3), and varying desorption with aq. NaCl (Table 1). These two observations, which lead to differential migration, have been applied for their separation.

The dye-mixture was added to the column (10 × 1 cm) packed with alumina (13 g) of *p*H 6.0 to a height of 8 cm, and kept for an hour. Aq. sodium chloride (*M*/100) was gradually added as eluting solvent. With 10 ml of the developer, two distinct bands, separated from each other (1.0 cm), were formed. OG was eluted out of the column with 30 ml of the eluent. The blue band of NB could be eluted out with 25 ml of aq. sodium sulphate (*M*/100).

The recoveries were quantitative.

The surface area of the alumina samples was determined to be 80-90 m^2/g (BET method). As the turning point in the adsorption isotherms is not well-defined, coverage factor (C.F.) could not be determined. However, if the relationship – C.F. $= 1.2 \times 10^{-7}$ (ionic weight)$^{2.93}$ is considered[6], the

C.F. of OG and NB is computed to be 2.8 and 14.3 respectively. It is observed that the dyes travel in the order of decreasing C.F.

References

1. G. L. MUNDHARA and J. S. TIWARI, *J. Indian Chem. Soc.*, 1978, **55**, 1032.
2. G. L. MUNDHARA and J. S. TIWARI, *J. Indian Chem. Soc.*, 1979, **56**, 737.
3. M. P. TIWARI, J. S. TIWARI and G. L. MUNDHARA, *J. Indian Chem. Soc.*, 1980, **57**, 806.
4. E. GURR, "Synthetic Dyes in Biology, Medicine and Chemistry", Academic Press, 1971, p. 576.
5. C. H. GILES, A. P. D'SILVA and A. S. TRIVEDI, *J. Appl. Chem.* (London), 1970, **20**, 37.
6. L. BOOSENS, *Industrie Chim. Belge.*, 1952, **17**, 211.

J. Indian Chem. Soc.,
Vol. LVII, April 1980, pp. 408-410

Synthesis and Spectral Studies of Triphenylantimony(V) Oximates and Benzamidoximate

V. K. JAIN, R. BOHRA and R. C. MEHROTRA*

Chemical Laboratories, Rajasthan University, Jaipur-302 004 (India)

Manuscript received 29 October 1979, accepted 28 December 1979

Complexes of the general formula, $Ph_3Sb(ONCRR')_2$ (where R and R' = Me, Me ; Me, Et ; Me, Pr ; Me, Ph ; Et, Et ; Et, Pr and NH_2, Ph), have been synthesised and characterised. A trigonal bipyramidal geometry has been suggested for these complexes. They can be purified by recrystallization and on distillation under reduced pressure, they yield triphenylantimony.

THERE has been a considerable interest in the Chemistry of organoantimony(V) complexes in recent years[1-3]. Significant changes in bonding and stereochemistry have been observed in a number of organoantimony derivatives on increasing the alkyl or aryl component on antimony atom[4-7]. Except a preliminary report[8] on triphenylantimony(V) diacetaldoximate, no study appears to have been made on antimony(V) oximates. In this communication, we report the synthesis and spectroscopic studies of oximates and benzamidoximate of triphenylantimony(V).

Experimental

Special precautions were taken to exclude moisture. Benzene and isopropanol were dried by usual method. $Ph_3Sb(OMe)_2$ was prepared by the reaction of triphenylantimony dichloride with sodium methoxide in methanol[4]. Oximes were prepared using standard techniques and were purified by careful fractionation[9].

Molecular weight, were determined cryoscopically in freezing benzene. IR spectra were recorded on Perkin-Elmer 577 spectrophotometer in the range of 4000-200 cm^{-1} using CsI optics. PMR spectra were run on a Perkin-Elmer R12B spectrometer working at 60MHz, in $CDCl_3$ solutions using TMS as an external standard.

Reaction between Ph_3SbCl_2 and Sodium Salt of Methyl Ethyl Ketoxime in 1 : 2 Molar Ratio :

Triphenylantimony dichloride (2.90 g) was added to the suspension of the sodium salt of methyl ethyl ketoxime (prepared from 0.33 g sodium and 1.20 g ligand) in benzene. Reactants were refluxed for about two hours. Sodium chloride was filtered off. Filtrate was evaporated under vacuum giving white solid product. The compound was recrystallized by dissolving in ~3 ml benzene and keeping the whole solution in the freezer for a night after adding ~25 ml light petroleum. Crystals so obtained were dried under vacuum. Yield ~35% and M.P. 65-66°. Anal. Found : C, 60.12 ; H, 6.29 ; N, 5.40 ; Sb, 23.64%. $Ph_3Sb(ONCMeEt)_2$. Calcd. : C, 59.45 ; H, 5.95 ; N, 5.33 ; Sb, 23.18%.

Other complexes were prepared in a similar manner and are summarized in Table 1.

Distillation of $Ph_3Sb(ONCMe_2)_2$:

$Ph_3Sb(ONCMe_2)_2$ (2.88 g) was heated at 0.4 mm pressure. At about 180° bath temperature a yellow crystalline product (0.17 g) b.p. 50-55° was collected. On increasing the bath temperature (180-230°) another fraction (1.36 g) was obtained, b.p. 165-66°. The latter compound, a viscous liquid, was further purified by redistillation in quantitative yield. This product was solidified by adding a crystal of triphenylantimony. Anal. of low boiling component (50-55°/0.4 mm) Found : N, 18.13% m.p. 58-60°. Me_2CNOH. Calcd. : N, 19.18%, m.p. 59°. Anal. of high boiling component (165-66°/0.4 mm) Found : C, 61.83 ; H, 4.34 ; Sb, 34.14%. Ph_3Sb. Calcd. : C, 61.23 ; H, 4.28 ; Sb, 34.49%.

Results and Discussion

Triphenylantimony(V) diketomixates of the type, $Ph_3Sb(ONCRR')_2$, may be prepared from the following reactions :

$$Ph_3Sb(OMe)_2 + 2Me_2CNOH \xrightarrow[\Delta]{\text{Benzene}} Ph_3Sb(ONCMe_2)_2 + 2MeOH$$

* Present address : Vice Chancellor, Delhi University, Delhi (India).

TABLE 1—REACTIONS OF TRIPHENYLANTIMONYDICHLORIDE WITH SODIUM SALT OF OXIMES

Reactants (g) R'R>C=NOH (R & R' =)	Sodium Metal	Ph_3SbCl_2	Product and %yield of Recrystallised Product	M.P. (°C)	%Analysis Found (calc) C	H	Sb	N	IR Assignments** νC=N cm⁻¹	%Yield of Triphenylantimony on Distillation (B.P.°C/mm)
Me,Me 0.85	0.27	2.45	$Ph_3Sb(ONCMe_2)_2$ ~78	116	55.54 (57.97)	4.74 (5.47)	24.81 (24.52)	5.88 (5.68)	1645m 1615m	~53 (165-66/0.4)
Et,Me 1.20	0.33	2.90	$Ph_3Sb(ONCMeEt)_2$ ~35	65-66	60.12 (59.45)	6.29 (5.95)	23.64 (23.78)	5.40 (5.38)	1620w	~39 (178/1.0)
Me,Pr 1.44	0.34	3.00	$Ph_3Sb(ONCMePr)_2$ ~18	81-82	59.47 (60.77)	6.47 (6.38)	22.34 (22.00)	5.02 (5.06)	1605w	~49 (155-56/0.05)
Me,Ph 1.59	0.28	2.49	$Ph_3Sb(ONCMePh)_2$ ~38	150-54	65.11 (65.72)	4.81 (5.03)	20.27 (19.60)	4.25 (4.51)	1580m	~12 (160-64/0.4)
Et,Et 1.34	0.31	2.80	$Ph_3Sb(ONCEt_2)_2$ ~50	64	60.01 (60.77)	6.85 (6.38)	22.39 (22.00)	4.90 (5.06)	1645vw 1615vw	~41 (162-64/0.3)
Et,Pr 1.50	0.31	2.77	$Ph_3Sb(ONCEtPr)_2$ ~54	90-91	61.43 (61.98)	7.29 (6.76)	22.70 (20.94)	4.77 (4.82)	1602w	~38 (165-/0.3)
Ph(NH₂)>C=NONa 1.71		2.61	$Ph_3Sb(ONCNH_2Ph)_2$ ~98	143-4	60.98 (61.65)	4.23 (4.69)	18.89 (19.58)	8.55 (8.99)	1605s	~16 (160/1.0

** Where s=strong, m=medium, w=weak and vw=very weak.

$$Ph_3SbCl_2 + 2Me_2CNOH + 2Et_3N \xrightarrow[\Delta]{\text{Benzene}} Ph_3Sb(ONCMe_2)_2 + 2Et_3N.HCl$$

$$Ph_3SbCl_2 + 2NaONCRR' \xrightarrow[\Delta]{\text{Benzene}} Ph_3Sb(ONCRR')_2 + 2NaCl$$

(where R and R' = Me, Me ; Me, Et ; Me, Pr ; Me, Ph ; Et, Et ; Et, Pr and NH_2, Ph).

All these compounds are white crystalline solids and can be recrystallized from benzene light petroleum mixture. They are hydrolytically unstable and are soluble in common organic solvents. Cryoscopic molecular weight determinations of some of these complexes indicate that they are monomeric in benzene.

A weak broad band in the region 3000-3380 cm⁻¹, which has been assigned to the intramolecularly hydrogen bonded OH in free oximes[10], is absent in the IR spectra of these complexes. Compared to νC=N vibration at ~1668 cm⁻¹ in the free oximes, two νC=N vibrations at ~1640 cm⁻¹ and 1615 cm⁻¹ have been observed in the complexes of the type $Ph_3Sb(ONCRR')_2$ (where R=R'=Me or Et). In cases, where R≠R', only one C=N stretching vibration has been observed in the region 1620-1580 cm⁻¹. A lowering of about 30-40 cm⁻¹ may be ascribed to the stabilization of C=N bond by resonance[11] with non-bonding electron pair on oxygen atom of the imino group. Removal of hydrogen by more electropositive antimony may favour the structure $\begin{matrix}R \\ R'\end{matrix}\!\!>\overset{-}{C}\!-\!N\!=\!\overset{+}{\ddot{O}}\!-$ which should result in a decrease of C=N frequency due to partial attainment of single bond character[12,13]. Alternatively, this type of lowering may also be ascribed to the mass effect[14].

Two bands at 3460 and 3360 cm⁻¹ in $Ph_3Sb(ONCNH_2Ph)$ have been assigned for free amino group. A down-field shift in C=N stretching by ~35 cm⁻¹ has also been observed in this complex.

In all these complexes the N–O stretching vibrations of the ligands shift towards lower frequencies by 10-20 cm⁻¹. νSb–O stretchings occur in the region 380-420 cm⁻¹ [15-17].

The PMR spectra of $Ph_3Sb(ONCMe_2)_2$ and $Ph_3Sb(ONCEt_2)_2$ show that resonances of protons on carbon atoms adjacent to the >C=N–O— group appear twice with equal intensity under normal conditions in $CDCl_3$. This may be expected, since the two radicals bound to this group are not equivalent because of the non-linearity of the >C=N–O group[12,18,19]. The PMR spectra of the complexes, $Ph_3Sb(ONCRR')_2$, in which R and R' attached to the imino carbon atom are different, exhibit only one type of proton resonances at room temperature. This may suggest that at ambient temperature both oximate groups are equivalent in these complexes because of free rotation around Sb–O bonds. Following (Fig. 1.) confirmation may be assumed for such complexes.

These complexes resemble common alkoxides and carboxylates in some of the properties, the latter are all penta-coordinated with trigonal

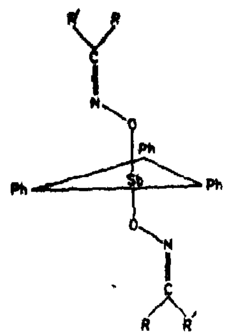


Fig. 1

bipyramidal geometry in which more electronegative substituents occupy the apical positions with three phenyl groups at equitorial positions[20-23]. By analogy to these compounds, we may assume that these complexes may also have a trigonal bipyramidal geometry in which two oxygen atoms occupy apical positions (Fig. 1.)

Thermal Decomposition :

A different type of thermal decomposition has been observed in these complexes which is not observed hitherto in the triorganoantimony(V) compounds[24]. When these complexes are heated under vacuum (0.1-1.0 mm) at about 170-230°, two products distilled out along with a black residue in distillation flask. The nature of the first product, a low boiling component obtained in a very poor yield, varies with the nature of the ligand. In case of $Ph_3Sb(ONCMe_2)_2$, nitrogen analysis, m.p. and i.r. spectra of low boiling component correspond to the free oxime. The second, high boiling component, obtained as a viscous mobile liquid contains some nitrogenous impurities from which it can be purified by redistillation. It has been identified as triphethylantimony. This mobile liquid can immediately be crystallized out (m.p. 47-48°) by adding a crystal of triphenylantimony. The IR spectra is similar in finger print region to that of triphenylantimony. PMR spectra exhibit only phenyl group resonances at 7.40-7.47 δ in CCl_4.

Acknowledgement

One of the authors (V.K.J.) is grateful to the University Grants Commision, New Delhi for the award of Junior Research Fellowship under Special Assistance Programme.

References

1. J. N. R. Ruddick and J. R. Sams, *J. Organometal. Chem.*, 1977, **128**, 041.
2. R. A. Labes and A. Schmidt, *Z. Anorg. Allg. Chem.*, 1976, **425**, 117.
3. H. A. Meinema and J. G. Noltes, *J. Organometal. Chem.*, 1976, **107**, 249.
4. W. E. McEwen, G. H. Briles and B. E. Giddings, *J. Amer. Chem. Soc.*, 1969, **91**, 7079.
5. H. A. Meinema and J. G. Noltes, *J. Organometal. Chem.*, 1972, **36**, 313.
6. H. A. Meinema, A. Macker and J. G. Noltes, *J. Organometal. Chem.*, 1972, **37**, 285.
7. G. Ferguson and D. M. Hawley, *Acta Crystal., Sect.* B 1974, **30**, 103.
8. P. G. Harrison and J. J. Zuckerman. *Inorg. Nuclear Chem., Letters*, 1970, **6**, 5.
9. R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Synthetic Identification of Organic Compounds", Wiley, New York 1956.
10. R. E. Rundle and M. Parsole, *J. Chem. Phys.*, 1952, **20**, 1487.
11. R. A. Krause, N. B. Colthup and D. H. Busch, *J. Phys. Chem.*, 1961, **65**, 2216.
12. J. R. Jennings and K. Wade, *J. Chem. Soc.*, A 1967, 1333.
13. I. Pattison and K. Wade, *J. Chem. Soc.*, A 1968, 2618.
14. P. G. Harrison and J. J. Zuckerman, *Inorg. Chem.*, 1970, **9**, 175.
15. R. G. Goel, *Canad. J. Chem.*, 1969, **47**, 4607.
16. R. G. Goel and H. S. Prasad, *Inorg. Chem.*, 1972, **11**, 2141.
17. E. Mislowsky Jr., *J. Organometal. Chem.*, 1974, **70**, 153.
18. E. Lustig, *J. Phys. Chem.*, 1961, **65**, 491.
19. J. V. Hatton and R. E. Richards, *Mol. Phys.*, 1962, **5**, 153.
20. K. Shen, W. E. McEwen, S. J. LaPlaca, W. C. Harnilton and A. P. Wolf, *J. Amer. Chem. Soc.*, 1968, **90**, 1718.
21. L. Kolditz, M. Gitter and E. Rosel, *Z. Anorg. Allg. Chem.*, 1962, **316**, 270.
22. H. C. Clark and R. G. Goel, *Inorg. Chem.*, 1966, **5**, 998.
23. M. Shindo and R. Okawara, *J. Organometal. Chem.*, 1966, **5**, 537.
24. G. O. Doak and L. D. Freedman, "Organometallic Compounds of Arsenic, Antimony and Bismuth", Wiley Interscience, 1970.

J. Indian Chem. Soc.,
Vol. LVII, April 1980, pp. 411-413

Indirect Spectrophotometric Method for Determination of Vanadium in High Speed Steel

N. K. BAISHYA* and D. BARKATAKI

Department of Chemistry, University of Gauhati, Gauhati-781 014, Assam

Manuscript received 7 November 1979, accepted 20 December 1979

An indirect spectrophotometric method for the determination of vanadium based on reduction of Fe(III) to Fe(II) by V(IV), and subsequent formation of ferrous-2,2'-dipyridyl complex was developed. The method was sensitive and was found suitable for determination of vanadium in ores and alloys.

SEVERAL methods[1-5] have been reported for the spectrophotometric determination of vanadium. Some of these methods, though fairly sensitive and useful, are not entirely adequate because of lack of their selectivity. Direct determination of vanadium in presence of common interfering ions is thus unsatisfactory. Benzophenyl hydroxylamine(BPHA) has been reported[6,7] to be highly specific for vanadium and has been used for its separation and spectrophotometric determination. However, the extractive spectrophotometric method for determination of vanadium using BPHA appears to be less sensitive because of low molar absorptivity of the BPHA complex.

It has been well established[8-10] that vanadium(IV) is a strong reductant and is oxidised in acid solution at room temperature by iron(III) quantitatively. Furthermore, it is known that vanadium(V) is quantitatively reduced to vanadium(IV) on heating with concentrated HCL.

$$V(IV)+Fe(III)=V(V)+Fe(II) \quad \ldots \quad (1)$$

$$V_2O_5+10HCl=2VCl_4+Cl_2+5H_2O \quad \ldots \quad (2)$$

Based on these facts West and Conrod[11] developed an indirect spot test method for detection of vanadium which was subsequently used for the indirect colorimetric[12,13] and also spectrophotometric[14] determination of vanadium using 2,2'-dipyridyl and 1,10-phenanthroline respectively. On the basis of the aforesaid principle, we investigated the possibility of using 2,2'-dipyridyl in the indirect spectrophotometric determination of vanadium. A satisfactory method was thus evolved which could find useful application in the determination of vanadium in ores and alloys.

Experimental

Apparatus : Absorbance measurements were made with a Beckman DK-2 Spectrophotometer.

Reagents : Aqueous solutions of the following reagents, prepared in distilled water, were used during the course of investigation. 2,2'-dipyridyl : A 0.2% solution of A. R. 2,2'-dipyridyl. Sodium nitrite : A 10% solution of B.D.H. grade sodium nitrite. Ferric chloride : A 0.1% solution of B.D.H. grade ferric chloride. Sodium phosphate : A 10% solution of A.R. sodium phosphate. Ammonia solution : A dilute solution of ammonia was prepared from liquor ammonia by diluting it in the proportion 1 : 2 with distilled water.

Standard Solution : A. R. ammonium metavanadate was used for preparing a standard stock solution. A 0.01*M* solution prepared initially in distilled water was used in the experiment after appropriate dilution.

Besides, a number of solutions of other metal ions were prepared to study their effect in the determination of vanadium, and the compounds used for the purpose of preparing these solutions were : $CaCO_3$, $MgCO_3$, $CuSO_4.5H_2O$, $ZnSO_4.7H_2O$, $MnSO_4.5H_2O$, $Ni(NH_4)_2(SO_4)_2.6H_2O$, $Pb(NO_3)_2$, $Fe(NH_4)(SO_4)_2.12H_2O$, $CdSO_4$, $PdCl_2$, K_2-$(PtCl_6^-)$, Na_2MoO_4, Na_2WO_4, $Cr_2(SO_4)_3$, $H_2C_2O_4$, tartaric acid and citric acid.

Procedure for Calibration : To different aliquots of a standard solution containing 15 to 120 micro gram of vanadium, 0.5 ml of concentrated HCl and 2 ml of 10% sodium nitrite solutions were added and the resulting solutions were allowed to stand for 10 minutes. Each of these solutions was then shaken with 0.5 gram of urea and was allowed to stand with occasional shaking for another 15 minutes. *p*H of these solutions were then adjusted between 5 and 6 by adding the required quantity of diluted ammonia solution (the amount of ammonia solution required was determined previously by titration of one of the above solutions to the methyl orange end point, subsequent *p*H measurement on which showed a *p*H slightly greater than 5). To

these solutions were then added 2 ml of 0.1% $FeCl_3$ solution followed by addition of 5 ml of 0.2% 2,2'-dipyridyl reagent and 1 ml of 10% sodium phosphate solution. Finally, the volume in each was made up to 25 ml in standard flasks and absorbance was measured at 520 nm after allowing it to stand for 30 minutes. A plot of absorbance values of these solutions against concentration of vanadium showed linear variation.

Experiment on the Study of Interferences: For studying the interference effect of each metal ion in their different mole ratios to vanadium viz. 10 : 1, 1 : 1 and 1 : 10, appropriate volume of the solution of the metal ion under investigation was added separately to each of the three 2 ml of 0.0005*M* solution of vanadium. The colour in each of these solutions was then developed by the procedure given above and the absorbance was measured at 520 nm. The colour in 2 ml of 0.0005 *M* vanadium solution in absence of any other metal ions was similarly developed and its absorbance too was measured at 520 nm for comparison.

Determination of vanadium in high speed steel: About a gram of the high speed steel sample (No. 64b), procured from the Bureau of Analysed Samples Ltd., was accurately weighed into a beaker and was dissolved by heating with 10 ml of 1 : 1 $HClO_4$ and 1 ml of concentrated HNO_3. Solution was then evaporated to dryness and to the dry mass was added sufficient 1 : 1 HCl to dissolve all soluble matters. The resulting solution along with precipitated tungstic acid was saturated with H_2S in a conical flask, and was subsequently heated on a water bath for complete precipitation of molybdenum. Mixed precipitate was then filtered through No. 40 Whatman filter paper and was washed with H_2S water. The filtrate after boiling off H_2S was made up to 250 ml in a standard flask.

An aliquot (0.5 to 2 ml) of the above solution was taken in a separating funnel and it was made 6*N* with respect to HCl by adding an equal volume of concentrated HCl. Solution was then shaken for 2-3 minutes with 5 ml of isobutyl methyl ketone. Aqueous layer was transferred to another separating funnel and two more extractions were done with isobutyl methyl ketone to reduce appreciably the concentration of iron in the aqueous layer. To the aqueous layer so obtained was added 1 ml of 5% tartaric acid to prevent interference due to chromium. The colour development and absorbance measurement in this solution was then made as described in the calibration procedure. Experiments were repeated with different aliquots of the same sample solution and also with different weighed samples of high speed steel. An average of a number of such determinations indicated the amount of vanadium present to be 1.93% as against 1.99% actually present.

Discussion

The indirect spectrophotometric method of determination of vanadium is virtually the method of determination of iron using 2,2'-dipyridyl. Vanadium(IV) obtained by the reduction of vanadium(V) with sodium nitrite and concentrated HCl is further oxidised quantitatively by iron(III) producing an equivalent amount of iron(II). Formation of 2,2'-dipyridyl complex with iron(II) which has long been known for colorimetric as well as spectrophotometric determination of iron can, thus, under the above situation provide a means for estimation of vanadium too. The molar absorptivity of ferrous-dipyridyl complex being higher than the BPHA method in the direct determination of vanadium, the method has greater sensitivity [0.0055 μg V cm^{-2}(520 nm)] than the BPHA method [0.0109 μg V cm^{-2}(510 nm)]. Thus inspite of the specificity of BPHA in the determination of vanadium, the present method can give better recovery of vanadium.

In the development of colour of the ferrous-dipyridyl complex, although a *p*H of 5-8 has been recommended, a slightly acidic *p*H between 5 and 6 is maintained to avoid precipitation of ferric hydroxide and phosphate, the latter resulting from the sodium phosphate added to mask the colour due to ferric ion.

An examination of the effect of the presence of other metal ions viz. Ca(II), Mg(II), Mn(II), Pd(II) and Pt(IV) revealed that these metal ions when present with vanadium in the mole ratio 10 : 1, 1 : 1 and 1 : 10 did not interfere. Fe(III) added (2 ml of 0.1% $FeCl_3$ solution) for oxidation of vanadium is in the mole ratio 10 : 1. The presence of iron in the mole ratio to the extent of 12 : 1 vanadium is tolerated. Zn(II) and Ni(II) although did not interfere when present in the mole ratio 1 : 1 and 1 : 10, they did interfere when present in the ratio 10 : 1. Other metal ions viz. Cu(II), Co(II), Cd(II), Cr(III), Mo(VI) and W(VI) interfered even when present in 1 : 10 ratio. Pb(II) in this proportion did not interfere but it did at higher concentrations. The presence of oxalic and citric acid retarded the development of colour of the ferrous dipyridyl complex. However tartaric acid did not have any adverse effect. In presence of Cr(III), precipitation occurred during colour development. Addition of 1 ml of 5% tartaric acid prevented precipitation and at the same time resulted in good recovery of vanadium.

The method has been tested for estimation of vanadium in standard sample of high speed steel and the recovery of vanadium was found to be good with an error within 3%.

Acknowledgement

The authors express their gratitude to Prof.

. N. Siddhanta for providing laboratory facilities carrying out this work.

eferences

1. E. R. WRIGHT and M. G. MELLON, *Ind. Eng. Anal. Ed.*, 1937, 9, 251.
2. N. A. TELVITE, *Anal. Chem.*, 1953, 25, 604.
3. A. K. DASGUPTA and M. M. SINGH, *J. Sci. Ind. Res*, 1952, 11B, 268.
4. W. M. WISE and W. W. BRANDT, *Anal. Chem.*, 1955, 27, 1392.
5. G. W. WALLACE and M. G. MELLON, *Anal. Chem.*, 1960, 32, 204.
6. U. PRIYADARSHINI and S. C. TANDON, *Anal. Chem.*, 1961, 33, 435.
7. S. C. SHOME, *Anal. Chem.*, 1951, 23, 1186.
8. G. JANTSCH and F. ZEMECK, *A. Analyst Chim.*, 1953, 139, 249.
9. E. EPHRAIM, *Helv. Chim. Acta*, 1931, 14, 1266.
10. A. GOTTLIEB, *Mikrochem. Mikroch, Acta*, 1951, 36/37, 871.
11. PH. W. WEST and L. J. CONROD, *Mikrochem, Ver. Mikrochim Acta*, 1950, 35, 443.
12. A. I. PONOMAREV and L. L. RATINA, *Zavodskaya lab.*, 1955, 21, 918.
13. I. P. ALIMARIN, *Zavodskaya Lab.*, 1940, 9, 5.
14. R. ROSOTTE and E. JAUDON, *Chim. Anal.*, 1954 36, 160.

J. Indian Chem. Soc.,
Vol. LVII, April 1980, pp. 414-416

Nitritometric Determination of Pharmaceutical Primary Arylamines Using Aminoanthraquinone Dyes as Internal Indicators**

R. RAMA KRISHNA, P. SIRAJ and C. S. PRAKASA SASTRY*

Department of Chemistry, Andhra University, Waltair-530 003

Manuscript received 21 June 1979, accepted 4 March 1980

A study has been made for the first time concerning the use of Sudan Blue GN, Sudan Green 4B, Alizarin Viridin, Alizarin Violet 3B or Alizarin Brilliant Violet R as an internal indicator in the nitritometric titration of aromatic primary amines such as sulphonamides (pure and in formulations), procaine, benzocaine and other compounds containing free arylamino group or yielding the same through hydrolysis or reduction. The end points are sharp and the results are accurate within ±0.2% on macro, ±0.4% on semimicro and ±2.5% on micro scale determinations. The titration procedures are simple and rapid.

RECENTLY we have reported the use of two aminoanthraquinone dyes, Oracet Blue B and Alizarin Brilliant Blue BS as internal indicators in the nitritometric determination of several aromatic primary amines[1]. Apart from these, no other aminoanthraquinone dye seems to have been reported as indicator either in acid-base or nitritometric assay of primary arylamines. Our investigations have now shown that the five aminoanthraquinone dyes, Sudan Blue GN (SB GN), Sudan Green 4B (SG 4B), Alizarin Viridin (AV), Alizarin Violet 3B (AV 3B) and Alizarin Brilliant Violet R (ABV R), (Colour Index Numbers: 61520, 61565, 62560, 60725 and 60730 respectively) can also be used as internal indicators in the nitritometric determination of several sulphonamides, local anaesthetics (procaine and benzocaine) and other drugs (pure and in pharmaceutical preparations) containing the free arylamino group or yielding the same by hydrolysis (phthalylsulphacetamide and phthalylsulphathiazole) or reduction (chloramphenicol). We have observed that these dyes can be successfully employed as internal indicators at room temperature in the titrations of sulphonamides which produce coloured diazonium salts as well unlike as many as the 15 internal indicators reported so far by several workers[2-9].

Experimental

Reagents :

All the sulphonamides, procaine, benzocaine and chloramphenicol were either I.P. or B.P. grade and their purity was checked by the B.P. methods[10].

0.2% solutions of all the aminoanthraquinone dyes obtained from M/s. Chroma-Gesellschaft were prepared in double distilled water excepting SB GN and SG 4B which were prepared with alcohol (0.2% solutions).

Sodium nitrite (BDH-AnalaR) solutions (0.05, 0.02 or 0.005 N) were prepared and standardised by the dead stop titration using the purified sulphanilic acid[10].

Always Basynth AR Hydrochloric acid was used.

Procedure for Compounds having Free Arylamino group :

An aliquot volume of the sample solution was treated with sufficient hydrochloric acid (1 :1) so as to maintain an overall acidity of 3.0-6.0 M in hydrochloric acid. 0.20-0.30 ml of 0.2% indicator solution was added and titrated slowly with sodium nitrite solution (0.05, 0.02 or 0.005 N), introducing the titrant under the surface of the solution with a burette having an elongated tip. In the vicinity of the end point, the tip was withdrawn, one or two drops of indicator solution added and the titration was completed by adding the titrant dropwise until a sharp colour change is obtained. The colour change at the end point is pink to green with SB GN, golden yellow to green with SG 4B, green to greenish yellow with AV or pinkish blue to blue with AV 3B or ABV R.

No indicator correction was necessary for the titrations with 0.1 N or 0.05 N sodium nitrite solutions. However, indicator correction was necessary in the usage of still lower concentrations of sodium nitrite solutions as three drops of SB GN, SG 4B or AV and AV 3B or ABV R solutions consume 0.04

** Presented at the 66th Indian Science Congress, held at Hyderabad, January, 1979.

ml and 0.20 ml of 0.005 *N* sodium nitrite solution respectively.

Procedure for Phthalylsulphacetamide and phthalylsulphathiazole :

The accurately weighed sample or the aliquot volume of the sample solution was boiled with 50 ml of dilute hydrochloric acid for 30 min under reflux condenser, cooled and completed the assay as mentioned above starting with the words "0.20 –0.30 ml of indicator......".

Procedure for Chloramphenicol :

About 0.25 g of chloramphenicol sample was accurately weighed, 10ml concentrated hydrochloric acid and in small portions 2.5 g of zinc dust were added and allowed to stand for one hour. Later it was filtered through cotton wool and washed the residue with water. The combined filtrate and washings were diluted to 50 ml and completed the assay as mentioned before.

Representative results from a large number of titrations in the determinations of sulphonamides, procaine, benzocaine and chloramphenicol in pure samples and pharmaceutical preparations were presented in Tables 1 and 2 using SB GN and AV as typical indicators.

Results and Discussion

The purity values obtained in the analysis of various sulphonamides, procaine, benzocaine and chloramphenicol using these five indicators were in good agreement with those values obtained by the official B.P. titrimetric procedures[10] (Table 2). As seen from the Tables 1 and 2, the methods were appeared to be simple with better than ±0.1%, 0.4% and 2.5% accuracies on macro, semimicro and micro scales respectively. These aminoanthraquinone dyes were found to be advantageous over the remaining internal indicators so far developed for two reasons. Estimations of sulphonamides which produce coloured diazonium salts can be carried out successfully as the diazonium salt colour does not interfere with the indicator colour change at the end point. The assay of sulphonamides, procaine and benzocaine at microgram level can also be carried out with reasonable accuracy. SB GN, SG 4B and AV were appeared to be better among the five dyes used. As the diazotisation process in considerably faster with the compounds estimated (Tables 1 and 2), addition of potassium bromide, sodium bromide or sodium nitrate to the reaction mixture during the titration is not necessary.

Interferences : The determinations were not affected by using these dyes as indicators, in the presence of reductants such as sulphurous acid, formic acid, hydroquinone even if they are present

TABLE 2—ASSAY OF SULPHONAMIDES IN PHARMACEUTICAL PREPARATIONS*

Name of the dosage from and the active substance	% Labelled amount		
	B.P. method	Proposed method**	
		SB GN	AV
Tablets :****			
Sulphaguanidine I.P.	99.85	99.86	100.90
Sulphadimidine I.P.	99 65	100.70	100.20
Sulphadiazine I.P.	98.70	100.10	100.10
Sulphamethoxypyridazine B.P.	100.10	100.15	100.05
Sulphasomidine B.P.	99.70	99.90	99.90
Sulphapyridine B.P.	99.70	99.85	99.90
Sulphadimethoxine B.P.	99.50	99.75	99.69
Phthalylsulphathiazole I.P.***	98.60	98.85	98.90
*Injections and eye drops*****			
Sulphadiazine injection B.P.	100.60	100.60	100.60
Sulphacetamide sodium I.P. eye drops	98.65	98.75	98.80

* Each result is an average of 5 separate analyses.
** Similar results obtained with SG 4B, AV 8B and ABV R.
*** After carrying hydrolysis.
**** These were market products of different manufacturers.

TABLE 1—ASSAY OF SULPHONAMIDES, PROCAINE BENZOCAINE AND CHLORAMPHENICOL*

Name of the compound	Maximum%error**					
	Sudan Blue GN			Alizarin Viridin		
	macro	semimicro	micro	macro	semimicro	micro
Sulphanilamide	0.08	0 20	1.4	0.10	0.30	1.8
Sulphacetamide	0.06	0.25	1.8	0 05	0.30	2.0
Sulphamethoxazole	0.20	0.30	1.6	0.08	0.35	2.2
Sulphamerazine	0.15	0.35	2.0	0.15	0.25	2.2
Sulphaphenazole	0.22	0.40	2.4	0.20	0.40	2.4
Procaine hydrochloride	0.15	0.25	1.8	0.18	0.25	1.6
Benzocaine	0.20	0.20	1.5	0.15	0.25	1.8
Phthalylsulphacetamide***	0.10	0.10	2.2	0.20	0.40	2.4
Chloramphenicol****	0.25	0.35	—	0.25	0.40	—

* Values obtained from at least six determinations.
** Similar results obtained with the other indicators, SG 4B, AV 8B and ABV R.
*** After carrying hydrolysis.
**** After carrying reduction.
Amount taken for, Macro : 250 mg, semimicro : 25 mg, micro : 250 µg.

in 10 fold molar excess with respect to the amine compound. Oxidising agents must be absent. Ca^{++}, Zn^{++}, ephedrine, codeine, sugar, lactose, starch, magnesium stearate, trimethoprim, adrenaline, alcohol or acetone usually present as adjuncts or binding materials in various pharmaceutical preparations of the amine compounds have no influence on the accuracy of the results.

The transition potentials (mv vs N.H.E.) for the sulphanilamide titration in 3.0 *M* hydrochloric acid medium are SB GN : 885 ± 10, SG 4B : 905 ± 15, AV : 900 ± 10, AV 3B : 930 ± 15 and ABV R : 935 ± 15.

We believe that, as all the five aminoanthraquinone dyes possess one or two secondary amino substituents, the colour change at the end point in the nitritometric assay may be due to the formation of N-nitroso compounds.

Acknowledgement

Thanks are due to Messrs Dolphin Laboratories and Smith, Stainstreet and Co., Calcutta ; Roche Products,

Ciba-Geigy, German Remedies and Cyanamid (India) Limited, Bombay ; IDPL, Warner-Hindustan, Hyderabad ; May and Baker, Madras, for the generous gifts of the sulphonamides used in these investigations and also to the authorities of Andhra University and CSIR, New Delhi, for the award of Research Fellowships to R.R.K. and P.S. We are also indebted to M/s. Chroma-Gesellschaft, Stuttgart for the generous gifts of the dyes used in the investigation.

References

1. R. R. Krishna, P. Siraj and C. S. Prakasa Sastry, *Acta Ciencia Indica*. 1978, **4**, 346.
2. H. F. Frost, *Analyst*, 1943, **68**, 51.
3. A. Agren, *Svensk. Farm. Tids.*, 1951, **55**, 229 through *Chem. Abs.*, 1951, **45**, 6187c.
4. R. Vasiliev, A. Cosmin and I. Burnea, *Rev. Chim.*, 1966, **17**, 174 through *Chem. Abs.*, 1966, **65**, 5808.
5. W. M. Banick and J. R. Valentine, *J. Pharm. Sci.*, 1964, **53**, 1242.
6. L. N. Guseva, *Aptech. Delo.*, 1966, **15**, 32 through *Chem. Abs.*, 1967, **66**, 140161v.
7. A. I. El-Sebai, Y. A. Beltagy and R. Soliman, *Pharmazie*, 1971, **26**, 615 through *Chem. Abs.*, 1972, **76**, 6750k.
8. E. Szekely, A. Bandel and M. Flitman, *Talanta*, 1972, **19**, 1429.
9. R. R. Krishna, P. Siraj and C. S. Prakasa Sastry, *Indian J. Pharm Sci.*, 1978, **40**, 69.
10. *British Pharmacopoeia*, Her Majesty's Stationary Office, London, 1973, pages 94, 445 and 451.

J. Indian Chem. Soc.,
Vol. LVII, April 1980, pp. 417-419

Two New Saponins from the Root of *Amaranthus spinosus* Linn*

N. BANERJI

Indian Institute of Experimental Medicine, 4, Raja S. C. Mullick Road, Calcutta-32

Manuscript received 21 March 1979, accepted 4 March 1980

Phytochemical investigation on the root of *Amaranthus spinosus* Linn. revealed the presence of two new saponins (I and II). Structure of saponins I and II were assigned to be as β-D-glucopyranosyl (1→2)-β-D-glucopyranosyl (1→2)-β-D-glucopyranosyl (1→3)-α-spinasterol and β-D-glucopyranosyl (1→4)-β-D-glucopyranosyl (1→3)-α-spinasterol respectively.

AMARANTHUS spinosus Linn is an erect herb. Roots of the plant is reported[1,2] to be used in menorrhagia, gonorrhea, eczema, colic and as a lactagogue. Isolation of α-spinasterol, α-spinasterol-octacosanoate and a new saponin of oleanolic acid from this plant have already been reported[3,4]. Dried and powdered roots of the plant was extracted successively with pet ether (60-80)°, $CHCl_3$ and MeOH. The MeOH extract was reduced to smaller volume and kept in a freeze overnight, shining crystals of KNO_3 was filtered out and the filtrate was evaporated to dryness. From this portion two saponins (I and II) were isolated in pure form by using different chromatographic technique. In this paper structure elucidation of these two saponins are described.

Two new saponins (I and II) were crystallised from MeOH−$CHCl_3$ (2 : 1), m.p. 340°(d), $[\alpha]_D^{28} -51.1°$ (pyridine) and m.p. 290°, $[\alpha]_D^{28} -40.1°$ (pyridine) and analysed for $C_{47}H_{88}O_{16}$ and $C_{41}H_{78}O_{11}$ for saponins (I and II) respectively.

On complete acid hydrolysis with 7% H_2SO_4 the saponins yielded α-spinasterol, D-glucose and an artefact formed during acid hydrolysis which was identified as stigma-8(14), 22-dien-3β-ol[5]. Due to the formation of this compd., it was not possible to find out the molar ratios of aglycone : sugar present in these saponins by the method of complete acid hydrolysis. In order to calculate the molar ratios, a controlled method of hydrolysis was developed by using 0.02 $N-H_2SO_4$ for 45 minutes. Both the saponins, on controlled acid hydrolysis yielded α-spinasterol-β-D-glucopyranoside[6] and D-glucose in the molar ratio of 1 : 2 and 1 : 1 respectively.

The α-spinasterol-β-D-glucoside, $C_{35}H_{58}O_6$, have (M^+ 574), m.p. 284-86°, tetraacetate, m.p. 156-58°. Moreover, the MS of both the free glycoside and its tetraacetate showed fairly stable molecular ions and the spectrum of the acetate distinctly showing characteristic fragmentation of Δ^{22}-steroids and hexapyranoside tetraacetate. Also, the NMR spectrum (60 MHZ) of the tetraacetate showed the signal for C-5 sugar proton at δ3.62, considerably upfield from that of methyl-α-D-glucose tetraacetate[7]. The sugar linkage of this glucoside was thus assigned the β-configuration, since the C-5 proton signal in β-glucosides is known[8] to be shifted upfield from that in α-anomers and its remains uneffected[9] by the nature of the aglycone.

The saponins were completely methylated by Hakomori's method. Complete methylations were confirmed by IR spectra of the permethylated products. The permethylated saponin I on complet hydrolysis yielded 2, 3, 4, 6-tetra-*O*-methyl-β-D-glucose, m.p. 93-94°, $[\alpha]_D^{28}+83.2°$ (H_2O) (Lit.[11]. m.p. 96°, $[\alpha]_D+84°$) and 3, 4, 6-tri-*O*-methyl-β-D-glucose, m.p. 96-98°, $[\alpha]_D^{28}+79.2°$ (H_2O) (Lit.[12] m.p. 97-98° $[\alpha]_D+78.1°$) in 1 : 2 molar ratio. The permethylated saponin II on hydrolysis yielded 2, 3, 4, 6-tetra-*o*-methyl-D. Glucose and 2, 3, 6-tri-*O*-methyl-D-glucose m.p. 120-121° $[\alpha]_D^{28}+69.1°$ (H_2O) (Lit.[13] m.p. 121-123°, $[\alpha]_D+70°$) in the molar ratio of 1 : 1. Periodate oxidation of the saponins was carried out at room temperature using 0.1*M* sodium metaperiodate solution. Consumption of oxidant and liberation of formic acid were found to be 4.12 and 0.98 moles respectively for saponin I and 3.2 and 1.02 moles respectively for saponin II.

With regard to the configuration of saponin glycosidic linkages, it is a general observation that D-sugars occur with β-glycosidic and L-sugars with α-glycosidic linkages[14]. The calculation of molar rotation of the saponins on the basis of Klyne's rule[15] also spports the β-linkages. The calculated

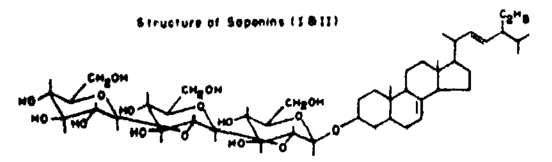
* Presented at the Annual Convention of Chemists, held at Andhra University, Waltair, India (Dec. 1978)

TABLE 1—MOLECULAR ROTATION CALCULATION OF SAPONIN I AND II

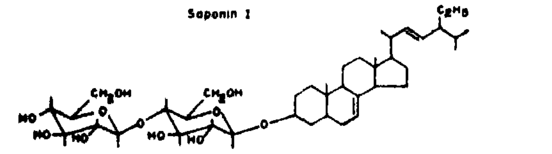
Compound	$[\alpha]_D$	$[M]_D$
	Lit. Value	
Methyl-β-D-glucopyranoside	−34.2°	−66°
	Observed value	
α-Spinasterol-β-D-glucopyranoside	−35°	−200.1°
	Calculated value	
For Saponin I	—	−332°
For Saponin II	—	−266°
	Observed value	
For Saponin I	51.1°	−463°
For Saponin II	40.1°	−299°

$[M]_D$ of saponin I and saponin II (Table 1) were −332° and −266° respectively which are in reasonable agreement with the observed value −463° and −299° respectively. Hence the structures of saponin I and saponin II can be represented as follows :

Structure of Saponins (I & II)



Saponin I



Saponin II

Experimental

All specific rotations are equilibrium values. All evaporations were carried out in vacuum at 35-40°. Whatman No. 1 paper was used for analytical paper chromatography and Whatman No. 3 MM paper for preparative chromatography.

The solvent mixture (v/v) used for partition chromatography of sugars were : A, *n*-butanol : acetic acid : water (4 : 1 : 5) ; upper layer ; B, *n*-butanol : pyridine : water (6 : 4 : 3) ; C, ethyl acetate : pyridine : water (8 : 2 : 1). Spray reagents were (a) aqueous saturated aniline oxalate and (b) alkaline silver nitrate solution.

Isolation of Saponin (I and II) :

Dried and powdered root (5 kg) of the plant was extracted successively with petroleum ether (60-80°), $CHCl_3$ and MeOH. The methanol extract of the roots was reduced to a smaller volume, and kept in a freeze overnight. Shining crystal of KNO_3 was filtered out and the filtrate was evaporated to dryness. The brown solid obtained gave positive test for saponins when shakes with water. The material was dissolved in *n*-butanol and acetone was added to this solution when a brown precipitate was obtained. The pale-yellow amorphous powder was isolated by centrifugation. The powder was resolved in three components by TLC on a silica gel G plate using a solvent system prepared by addition of MeOH to a mixture of 2 ml H_2O and 30 ml $CHCl_3$ till the whole was clear. The mixture was chromatographed on a silica gel column and saponins (I and II) were eluted with MeOH : $CHCl_3$ = 10 : 90 and 8 : 92 respectively. The pure saponins (I and II) were crystallised from $CHCl_3$: MeOH mixture having m.p. 304°(d), $[\alpha]_D^{28}$ −51.1° (c, 1 in pyridine) for saponin I and m.p. 290°, $[\alpha]_D^{28}$ −40.1° (C, 1.5 in pyridine) for saponin II and analysed for $C_{47}H_{88}O_{16}$ and $C_{41}H_{78}O_{11}$ for saponins (I and II) respectively.

Identification of Aglycone and Sugars :

Hydrolysis of saponins I and II with 7% H_2SO_4 yielded α-spinasterol, m. p. 168-70°, $[\alpha]_D^{27}$ −3.8° ($CHCl_3$). Superimposable IR spectra and mixed melting point suggested its identity with α-spinasterol. Stigmasta-8 (14), 22-dien-3β-ol, obtained by acid hydrolysis, separated from α-spinasterol by chromatography of the acetate over $AgNO_3$ (15%) impregnated silica gel. Stigmasta-8(14), 22-dien-3β-yl acetate was crystallised from MeOH m.p. 136-37°, $[\alpha]_D^{27}$ −42° ($CHCl_3$) ; ν_{max}^{Nujol} 1730, 1250(OAC), 970 (H)C=C(H) cm^{-1}. MS : *m/e* (rel. intensity 454 (M^+, 8), 439(2), 411(2), 394(79), 379(8), 351(12), 342(2), 313(25), 282(12), 273(4), 255(62), 228(12), 213(16), NMR: (δ in $CDCl_3$) 0.78(18-Me), 0.91 (19-Me), 1.08d (21-Me), 0.86-1.08 m (25-Me, 26-Me, 29-Me), 2.08(OAC), 4.73 m (H-3), 5.30m (H-22, H-23). (Found : C, 82.20, H, 11.35. Calc. for $C_{31}H_{50}O_2$: C 81.93, H, 11.01%). The sugars in aqueous portion were identified as D-glucose by paper chromatography (solvent systems A, B and C).

Partial Hydrolysis of Saponins I and II :

200 mg of each of the saponins was hydrolysed with 0.02*N* N_2SO_4(50 ml) for 45 minutes. Both the saponins yielded α-spirasterol-β-D-glucopyranoside and D-glucose. Gravimetric estimation of α-spinasterol-β-D-glucoside and spectrophotometric estimation of D-glucose, showed the molar ratio of glucoside : glucose 1 : 2 and 1 : 1 in saponins I and II respectively. α-Spinasterol-β-D-glucoside were crystallised from C_6H_6 − EtOH, m.p. 284-86°, $[\alpha]_D^{28}$ -35° (pyridine) ; ν_{max}^{Nujol} 32 0(OH) 970 cm^{-1}, MS : m/e (rel.intensity) 574 (M^+1.3), 559 (0.3), 556(0.1),

531(0.3), 433(4), 412(16), 394(40), 379(10), 369(6), 351(12), 300(10), 2›9(9), 273(15), 271(43), 255(65), 253(32) and 55(100) (Found : C, 72.0 ; H, 10.5, Calc. for $C_{36}H_{58}O_{6}$: C, 73.1, H, 10.1%.

Permethylation of Saponins I and II :

50% NaH disppersion in oil (ca. 250 mg) was suspended in DMSO (25 ml) and kept in an oil bath at 80° for 1 hr. A solution of saponins (150 mg) in DMSO (5 ml) was then added gradually and the mixture was kept at 80° for 1 hr with constant stirring. It was cooled in ice and MeI (3 ml) was added in drops. The fully methylated product isolated in the usual way showed no absorption band in the region of 3500-3600 cm^{-1} in IR. The permethylated saponin I on complete acid hydrolysis with $N-H_2SO_4$ yielded 2, 3, 4, 6-tetra-*o*-methyl-β-D-glucose m.p. 93-94°, $[\alpha]_D^{28}+83.2°$ (H_2O) and 3, 4, 6-tri-*o*-methyl-D-glucose, m.p. 96-98°, $[\alpha]_D^{27}+79.2°$ (H_2O) in 1 : 2 molar ratio. The permethylated saponin II on acid hydrolysis in the same way, yielded 2, 3, 4, 6-tetra-*o*-methyl-D-glucose and 2, 3, 6-tri-*o*-methyl-D-glucose, m.p. 120-21°, $[\alpha]_D^{28}+69.1°$ (H_2O) in 1 : 1 molar ratio. Molar ratio of the methylated sugars was determined by alkaline hypoiodite method[16].

Periodate-oxidation studies on saponin I and saponin II were carried out with 0.1*M* sodium metaperiodate solution. Consumption of the oxidant was determined spectrophotometrically[17] and was found to be 4.12 and 3.2 moles for saponins I and II respectively. The liberation of formic acid were estimated in the usual way[18] and were found to be 0.98 and 1.02 moles for saponins I and II respectively.

References

1. The Wealth of India (Raw materials), CSIR (New Delhi), 1948, Vol. I, 67.
2. R. N. CHOPRA, S. C. NAYAR, I. C. CHOPRA, Glossary of Indian Medicinal Plants, CSIR (New Delhi), 1956, 20.
3. N. BANERJI and R. N. CHAKRAVARTI, *J. Inst. of Chemists* (India), 1973, XLV, 205.
4. N. BANERJI, *Indian J. Chem.*, (in press).
5. L. H. ZAIKOW, G. A. CABOT, G. L. CHETTY, M. GHOSAL and G. KERN, *Tetrahedron Letters*, 1968, 5727.
6. Y. OBATA, S. SAKAMURA, M. KOSHIKA. *Bull. Agr. Chem. Soc.*, Japan, 1955, **19**, 189, *Chem. Abs.* 1956, **50**, 14247.
7. D. HORTON and H. LAUTERBACH, *J. Org. Chem.*, 1969, **34**, 86.
8. R. U. LEMIEUX and J. D. STEVENS, *Canad. J. Chem.*, 1965, **43**, 2059.
9. W. W. BINKLEY, D. HORTON, N. S. BHACCA, *Carbohydrate Res.*, 1969, **10**, 245.
10. S. HAKOMARI, *J. Biochem.*, 1964, **55**, 205.
11. J. C. IRVINE and E. L. HIRST, *J. Chem. Soc.*, 1922, **121**, 1213.
12. R. L. SUNDBERG, C. M. MCCLOSKEY, O. E. REES and G. H. COLEMAN, *J. Amer. Chem. Soc.*, 1945, **67**, 1080.
13. J. C. IRVINE and J. W. A. OLDHAM, *J. Chem. Soc.*, 1921, **119**, 1744.
14. S. RANGASWAMI and V. HARIHARAN, *Phytochem.*, 1970, **9**, 409.
15. W. KLYNE, *Biochem. J.*, 1950, **47**, XLI.
16. E. L. HIRST, L. HOUGH and J. K. N. JONES, *J. Chem. Soc.*, 1949, 928.
17. J. S. DIXON and D. LIPKIN, *Anal. Chem.*, 1954, **26**, 1092.
18. P. FLEURY and J. LANGE, *J. Pharm. Chem.*, 1952, **74**, 4770.
19. R. SESHADRI and S. RANGASWAMI, *Indian J. Chem.*, 1975, **13**, 447.

J. Indian Chem. Soc.,
Vol. LVII, April 1980, pp. 420-422

Some Fungicidal 3-Aryl/Aryloxymethyl-4-Aryl-5-Mercapto-1,2,4-Triazoles and *Bis*-(3-Aryloxymethyl-4-Aryl-1,2,4-Triazol-5-yl)-Methylene/Ethylene Disulphides

S. P. SUMAN and S. C. BAHEL*

Chemistry Department, University of Gorakhpur, Gorakhpur (U.P.)

Manuscript received 27 November 1978, revised 16 July 1979, accepted 4 March 1980

Eighteen 3-aryl/aryloxymethyl-4-aryl-5-mercapto-1,2,4-triazoles and twenty *bis*-(3-aryloxymethyl-4-aryl-1,2,4-triazol-5-yl)-methylene/ethylene disulphides have been prepared. All the compounds have been screened for their fungicidal activity against '*A. flavus*' and '*A. niger*' and were found to be antifungal.

3-AMINO-1,2,4-TRIAZOLE (Amizole) is a commercial herbicide. Several 1,2,4- and 1,3,4-triazoles and compounds containing triazole ring have been found to have bactericidal[1,2], fungicidal[3,4], insecticidal[5,6] and pesticidal[7,8] properties. With this in view, some title 1,2,4-triazoles have been prepared.

Heterocyclic sulphides have been reported to possess antitubercular, anticancer and antifungal[9] activities. The pesticidal screening results of *bis*-(4-aryl-5-mercapto-1,2,4-triazol-3-yl) alkanes have revealed that as the number of methylene group increased, activity increased in some respects[10]. A comparative study of pesticidal activity of mercapto compounds and their sulphides has shown that sulphides are relatively more active than parent mercapto compounds[11]. Hence, the title disulphides have also been prepared.

Experimental

All the melting points are uncorrected.

Aryl/aryloxyacetyl hydrazines :

These were prepared by the method of L. Conti[12].

3-Aryl/aryloxymethyl-4-aryl-5-mercapto-1, 2,4-triazoles[13] *:*

Aryl/aryloxyacetyl hydrazine (0.01*M*) and aryl isothiocyanate (0.012*M*) were dissolved in 8% aqueous sodium hydroxide (17.5 ml) and the mixture refluxed gently for five hours. It was poured into a large excess of water, stirred and then filtered. The filtrate was acidified with cold dilute hydrochloric acid. The precipitate obtained was filtered, washed and recrystallised from aqueous ethanol. The triazoles thus prepared are listed in Table 1.

Bis-*(3-aryloxymethyl-4-aryl-1,2,4-triazol-5-yl)-methylene/ethylene disulphides :*

To an ethanolic solution (20 ml) of 3-aryloxymethyl-4-aryl-5-mercapto-1,2,4-triazole (0.01*M*), fused sodium acetate (2.0 g) and methylene/ethylene dichloride (0.005*M*) were added. The contents were refluxed for four hours, cooled and then poured into water. The solid separated was filtered, washed and recrystallised from ethanol. The compounds thus prepared are listhed in Table 2.

TABLE 1—3-ARYL/ARYLOXYMETHYL-4-ARYL-5-MERCAPTO-1,2,4-TRIAZOLES

Compound number	Name	M.P. °C	Yield (%)
1.[a]	3-(4'-Chloro-3'-methylphenoxymethyl)-4-phenyl-5-mercapto-1,2,4-triazole	107	95
2.	3-(4'-Chloro-3'-methylphenoxymethyl)-4-*m*-chlorophenyl-5-mercapto-1,2,4-triazole	168	80
3.	3-(4'-Chloro-3'-methylphenoxymethyl)-4-*p*-chlorophenyl-5-mercapto-1,2,4-triazole	156	85
4.	3-(4'-Chloro-3'-methylphenoxymethyl)-4-*m*-tolyl-5-mercapto-1,2,4-triazole	122	75
5.	3-(4'-Chloro-3'-methylphenoxymethyl)-4-*p*-tolyl-5-mercapto-1,2,4-triazole	102	72
6.[b]	3-(2',4'-Dimethylphenoxymethyl)-4-phenyl-5-mercapto-1,2,4-triazole	111	84
7.	3-(2',4'-Dimethylphenoxymethyl)-4-*m*-chlorophenyl-5-mercapto-1,2,4-triazole	106	80
8.	3-(2',4'-Dimethylphenoxymethyl)-4-*p*-chlorophenyl-5-mercapto-1,2,4-triazole	110	82
9.	3-(2',4-Dimethylphenoxymethyl)-4-*m*-tolyl-5-mercapto-1,2,4-triazole	136	72
10.	3-(2',4'-Dimethylphenoxymethyl)-4-*p*-tolyl-5-mercapto-1,2,4-triazole	117	74
11.[c]	3-Benzyl-4-phenyl-5-mercapto-1,2,4-triazole	157	85
12.	3-Benzyl-4-*m*-tolyl-5-mercapto-1,2,4-triazole	48	78
13.	3-Benzyl-4-*p*-tolyl-5-mercapto-1,2,4-triazole	53	80
14.[d]	3-α-Naphthylmethyl-4-phenyl-5-mercapto-1,2,4-triazole	123	88
15.	3-α-Naphthylmethyl-4-*m*-chlorophenyl-5-mercapto-1,2,4-triazole	120	80

* Lecturer, Chemistry Department, Gorakhpur University, Gorakhpur.

(Table 1 Contd.)

16.	3-α-Naphthylmethyl-4-p-chlorophenyl-5-mercapto-1,2,4-triazole	129	87
17.	3-α-Naphthylmethyl-4-m-tolyl-5-mercapto-1,2,4-triazole	84.75	75
18.	3-α-Naphthylmethyl-4-p-tolyl-5-mercapto-1,2,4-triazole	91	80

All the compounds showed consistent nitrogen analysis.

IR Spectral data ν_{max} *in* cm^{-1}

a. 3325(–C=N–H) ; 1155(–C=S) ; 1050, 1250(=C–O–C–) ; 720, 750 (monosubstituted benzene ring) and 660 (C–Cl).

b. 3320 (–C=N–H) ; 1175(–C=S) ; 1050, 1260(=C–O–C–) and 720, 750 (monosubstituted benzene ring).

c. 3325(–C=N–H) ; 1170(–C=S) and 720, 750 (monosubstituted benzene ring).

d. 3320(–C=N–H) ; (1170–C=S) ; 1060, 1265(=C–O–C–), 1580 (Aromatic ring further conjugated) and 720, 750 (monosubstituted benzene ring).

TABLE 2 — *Bis*(3-ARYLOXYMETHYL)-4-ARYL-1,2,4-TRIAZOL-5-YL)-METHYLENE/ETHYLENE DISULPHIDES

Compound number	Name	M.P. °C	Yield (%)
19.	*Bis*-[3-(4′-chloro-3′-methylphenoxymethyl)-4-phenyl-1,2,4-triazol-5-yl]-methylene disulphide	179	70
20.	*Bis*-[3-(4′-chloro-3′-methylphenoxymethyl)-4-*m*-chlorophenyl-1,2,4-triazol-5-yl]-methelene disulphide	150	60
21.[e]	*Bis*-[3 (4′-chloro-3′-methylphenoxymethyl)-4-*p*-chlorophenyl-1,2,4-triazol-5-yl]-methylene disulphide	186	65
22.	*Bis*-[3-(4′-chloro-3′-methylphenoxymethyl)-4-*m*-tolyl-1,2,4-triazol-5-yl]-methylene disulphide	135	63
23.	*Bis*-[3-(4′-chloro-3′-methylphenoxymethyl)-4-*p*-tolyl-1,2,4-triazol-5-yl]-methylene disulphide	190	67
24.[f]	*Bis*-[3-(2′,4′-dimethylphenoxymethyl)-4-phenyl-1,2,4-triazol-5-yl]-methylene disulphide	132	75
25.	*Bis*-[3-(2′,4′-dimethylphenoxymethyl)-4-*m*-chlorophenyl-1,2,4-triazol-5-yl]-methylene disulphide	125	62
26.	*Bis*-[3-(2′,4′-dimethylphenoxymethyl)-4-*p*-chlorophenyl-1,2,4-triazol-5-yl]-methylene disulphide	137	68
27.	*Bis*-[3-(2′,4′-dimethylphenoxymethyl)-4-*m*-tolyl-1,2,4-triazol-5-yl]-methylene disulphide	120	65
28.	*Bis*-[3-(2′,4′-dimethylphenoxymethyl)-4-*p*-tolyl-1,2,4-triazol-5-yl]-methylene disulphide	176	70
29.[g]	1″,2″-*Bis*-[3-(4′-chloro-3′-methylphenoxymethyl)-4-phenyl-1,2,4-triazol-5-yl]-ethylene disulphide	121	67
30.	1″,2″-*Bis*-[3-(4′-chloro-3′-methylphenoxymethyl)-4-*m*-chlorophenyl-1,2,4-triazol-5-yl]-ethylene disulphide	110	59
31.	1″,2″-*Bis*-[3-4′-chloro-3′-methylphenoxymethyl)-4-*p*-chlorophenyl-1,2,4-triazol-5-yl]-ethylene disulphide	115	60
32.	1″,2″-*Bis*-[3-(4′-chloro-3′-methylphenoxymethyl)-4-*m*-tolyl-1,2,4-triazol-5-yl]-ethylene disulphide	96	60
33.	1″,2″-*Bis*-[3-(4′-chloro-3′-methylphenoxymethyl)-4-*p*-tolyl-1,2,4-triazol-5-yl]-ethylene disulphide	100	62
34.	1″,2″-*Bis*-[3-(2′,4′-dimethylphenoxymethyl)-4-phenyl-1,2,4-triazol-5-yl]-ethylene disulphide	78	71
35.[h]	1″,2″-*Bis*-[3-(2′,4′-dimethylphenoxymethyl)-4-*m*-chlorophenyl-1,2,4-triazol-5-yl]-ethylene disulphide	98	60
36.	1″,2″-*Bis*-[3-(2′,4′-dimethylphenoxymethyl)-4-*p*-chlorophenyl-1,2,4-triazol-5-yl]-ethylene disulphide	76	65
37.	1″,2″-*Bis*-[3-(2′,4′-dimethylphenoxymethyl)-4-*m*-tolyl-1,2,4-triazol-5-yl]-ethylene disulphide	45	62
38.	1″,2″-*Bis*-[3-(2′,4′-dimethylphenoxymethyl)-4-*p*-tolyl-1,2,4-triazol-5-yl]-ethylene disulphide	52	70

All the compounds showed consistent nitrogen analysis.

IR Spectral data ν_{max} *in* cm^{-1}

e. 1050, 1250(=C–O–C–), 650 (C–Cl) and 850 (*p*-disubstituted benzene ring).

f. 1060, 1250(=C–O–C–) and 720, 750 (monosubstituted benzene ring).

g. 1060, 1255(=C–O–C–), 720, 750 (monosubstituted benzene ring) and 665 (C–Cl).

h. 1055, 1260(=C–O–C–), 650(C–Cl) and 800 (*m*-substituted benzene ring).

Fungicidal activity :

All the compounds of Tables 1 and 2 have been screened for their antifungal activity against '*A. niger*' and '*A. flavus*' by agar plate technique[14,15] at three different concentrations namely, 1 : 1,000 ; 1 : 10,000 ; 1 : 1,00,000 and were found to be antifungal. Groups substituted at the position 4 (Table 1 and 2) had the following order for the fungicidal activity :

p-Chlorophenyl- > *m*-Chlorophenyl- > *p*-Tolyl- > *m*-Tolyl- > phenyl-

and the groups at the position 3 showed the following order :

4′-Chloro-3′-methylphenoxymethyl- > 2′,4′-Dimethylphenoxymethyl. Compounds of Table 2 were more fungicidal than their corresponding triazoles. The introduction of ethylene moiety in place of methylene one decreased the fungicidal activity.

Acknowledgement

Authors are thankful to Prof. R. P. Rastogi, Head, Chemistry Department, University of

Gorakhpur for departmental facilities. One of us (S. P. Suman) is thankful to S.C.S.T. (U.P.) for the award of a J.R.F.

References

1. S. C. BENNUR, V. B. JIGAJINNI and V. V. BADIGER, *Rev. Rouw. Chim.*, 1976, **21**, 757 ; *Chem. Abs.*, 1976, **84**, 74806j.

2. I. CHIYOMARA, F. YOSHINAGA and G. DOHKE, Jap. Pat., 7389, 400, 1973 ; *Chem. Abs.*, 1974, **81**, 73392m.

3. S. A. GREENFIELD, C. S. MICHAEL and W. C. VONMEYER, *Ger. Offen.* 1, 966, 806, 1974 ; *Chem. Abs.*, 1975, **82**, 150485l.

4. W. KRAEMER, K. H. BUECHEL, W. BRANDES and P. E. FROHBERGER, *Ger Offen.*, **2**, 334, 352, 1975 ; *Chem. Abs.*, 1975, **82**, 170967f.

5. G. TANAKA, Japan Kokai, 1974, 7495, 978 ; *Chem. Abs.*, 1975, **82**, 156320h.

6. T. L. WAKINS and D. M. WEIGHTON, *Ger. Offen.*, 2, 580, 287, 1976 ; *Chem. Abs.*, 1976, **84**, 135677f.

7. H. KRISTINSSON and K. RUEFENACHT, (Ciba-Geigy A. G.), *Ger. Offen* ; 2,330,606, 1974 ; *Chem. Abs.*, 1974, **80**, 95962d.

8. B. BOEHNER, W. MEYER and D. DOWES, *Swiss*, 1976, 573, 206 ; *Chem. Abs.*, 1976, **84**, 180182a.

9. C. R. MOLLER and V. BALIAH, *J. Amer. Chem. Soc.*, 1948, **70**, 3853.

10. CHIMETRON S. a.r.l., *Fr.* 1, 476, 548, 1967 ; *Chem. Abs.*, 1968, **69**, 96715p.

11. K. C. JOSHI and A. B. SEN, *J. Sci. Food Agric.*, 1952, **11**, 526.

12. L. CONTI, *Boll. Sci. Fac. Chim. Ind. Bologna*, 1964, **22**, 13-15 ; *Chem. Abs.*, 1977, **86**, 89 884w.

13. B. K. PAUL and U. P. BASU, *J. Indian Chem. Soc.*, 1969, **46**, 1121.

14. J. G. HORSHFALL, *Bot. Rev.*, 1945, **5**, 357.

15. U. S. D. A. CIRCULAR No. 193, 1931.

J. Indian Chem. Soc.,
Vol. LVII, April 1980, pp. 423-425

Possible Psychopharmacological Agents, Part XI* : Synthesis and CNS Activity of Some Fluorine Containing Indole Derivatives

KRISHNA C. JOSHI, VIJAI N. PATHAK and POORAN CHAND

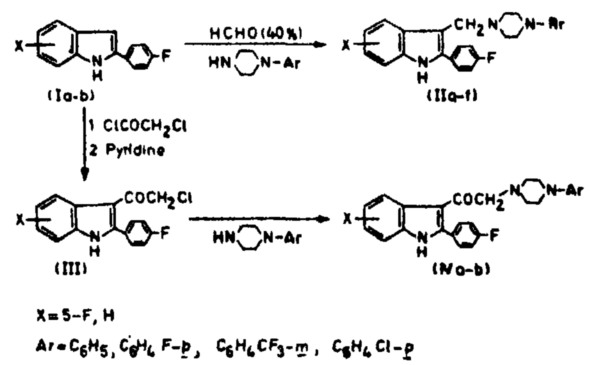
Department of Chemistry, University of Rajasthan, Jaipur-302 004 (India)

Manuscript received 8 August 1979, accepted 4 March 1980

2-(4'-Fluorophenyl)indole undergoes Mannich reaction with 1-arylpiperazines and formaldehyde (40%) to give the corresponding 3-(1-arylpiperazinomethyl)-2-(4'-fluorophenyl)indoles. 3-Chloroacetyl-2-(4'-fluorophenyl)indole produces 3-(1-arylpiperazinoacetyl)-2-(4'-fluorophenyl)indoles by the reaction of the corresponding 1-arylpiperazines. All the compounds have been characterized by IR, PMR and ^{19}F NMR spectral studies. Some compounds have been screened for CNS activity on different parameters.

THE indole derivatives are well known for their biological activities[1-4]. 3-[4(4'-Fluorophenyl)-1-piperazinomethyl]indole has shown good analgesic and antiinflammatory activities[5,6]. The introduction of fluorine or CF_3 group into an organic molecule increases its solubility in lipid material and fat deposits in the body[7]. 3-Dialkylaminoacetylindole derivatives have been reported to possess analgesic activity[8].

In view of this, we have now undertaken the synthesis of fluorine containing 3-(1-arylpiperazinomethyl)-2-(4'-fluorophenyl)indoles(IIa-f) by the Mannich reaction[9] of corresponding indoles(Ia-b) with arylpiperazines and formaldehyde (40%) in dioxane at 0° and 3-(1-arylpiperazinoacetyl)-2(4'-fluorophenyl)indoles(IVa-b) by the action of 1-arylpiperazines on 3-chloroacetyl-2-(4'-fluorophenyl)indole(III)[11,12] as CNS agents [Scheme I].



SCHEME-I

Experimental

Melting points of all the compounds are uncorrected. IR spectra have been recorded on Perkin-Elmer (model-557) in nujol mull. PMR(60 MHz) and ^{19}F NMR(56.4 MHz) spectra have been recorded on Perkin-Elmer (model RB-12). TMS was taken as internal standard for PMR spectra, and TFA was taken as external standard for ^{19}F NMR spectra.

2-(4'-Fluorophenyl)indole(Ia),5-fluoro2-(4'-fluorophenyl)indole(Ib) and 3-chloroacetyl-2-(4'-fluorophenyl)indole have been prepared by the method of Joshi *et al*[11,12].

3-(1-Arylpiperazinomethyl)-2-(4'-fluorophenyl)indoles(IIa-f)

A solution of 5-F/H-2-(4'fluorophenyl)indole (0.01 mole) in dioxane (20 ml) was added to a cooled solution of formaldehyde (0.01 mole, 40%) and appropriate phenylpiperazine (0.012 mole) in acetic acid (glacial; 5 ml) during 30 min. The whole reaction mixture was further stirred for 3-4 hrs at 0-5° and then diluted with water. It was filtered and the filtrate on basification afforded the desired compounds. The compounds were purified by recrystallization from ethanol and gave single spots on TLC (Table 1).

3-(1-Arylpiperazinoacetyl)-2-(4'-fluorophenyl)indoles(IVa-b) :

3-Chloroacetyl-2-(4'-fluorophenyl)indole(III, 0.01 mole) was refluxed with appropriate 1-arylpiperazine (0.015 mole) in ethanol for 3 to 4 hrs. The reaction mixture, on cooling, gave the desired compound which was filtered and recrystallized with ethanol. The compounds gave single spots in TLC.

The characteristic and analytic data are recorded in Table 1.

* Part X ; J. *Prakt. Chemie*, In press (1980).

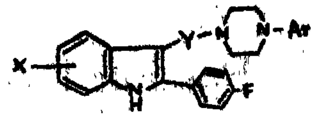


TABLE 1—CHARACTERISTIC AND ANALYTICAL DATA OF FLUORINE CONTAINING INDOLE DERIVATIVES

Sl. No.	X	Y	Substituent in Ar	Yield (% of theory)	M.P. °C	Molecular Formula*	% of Nitrogen Calcd.	% of Nitrogen Found
IIa	H	$-CH_2-$	4-F	62	170	$C_{25}H_{23}F_2N_3$	10.42	10.31
IIb	H	$-CH_2-$	4-Cl	59	159	$C_{25}H_{23}ClFN_3$	10.01	9.84
IIc	H	$-CH_2-$	H	61	189	$C_{25}H_{24}FN_3$	10.90	10.70
IId	H	$-CH_2-$	3-CF_3	58	187	$C_{26}H_{23}F_4N_3$	9.27	9.32
IIe	5-F	$-CH_2-$	3-CF_3	54	148	$C_{26}H_{22}F_5N_3$	8.91	8.68
IIf	5-F	$-CH_2-$	4-F	52	128-30	$C_{25}H_{22}F_3N_3$	9.97	9.82
IVa	H	$-COCH_2-$	H	58	188-89	$C_{26}H_{24}FN_3O$	10.17	9.84
IVb	H	$-COCH_2-$	4-Cl	68	177	$C_{26}H_{23}ClFN_3O$	9.38	9.12

* Satisfactory C and H analyses results were obtained.

IR (Nujol mull) cm^{-1} ; 3200-3400($>$NH), 1200-1400 (C – F stretching) and 1625-1640 (C=O in compound Nos. IVa and IVb).

PMR(TFA) δppm ; 7.8-8.2($>$NH), 3.9-4.1($-CH_2-N<\begin{smallmatrix}CH_2-CH_2\\CH_2-CH_2\end{smallmatrix}>N-$) and 4.3-4.4($-\overset{O}{\overset{\|}{C}}-CH_2-N<$ in compound Nos. IVa and IVb).

^{19}F NMR Acetone) ppm ; 39.0-42.0 (Ar-F), 49.0(5-F in compound Nos. IIe and IIf) and – 10.7(Ar – CF_3 in compound Nos. IId and IIe).

TABLE 2—GROSS ACTIVITY OF FLUORINE CONTAINING INDOLE DERIVATIVES

Compd. Sl. No.	Dose mg/kg	Gross Behaviour: SMA	Respiration	Reactivity: Sound	Reactivity: Touch	Writhing	Ataxia	Catalepsy	Convulsions	Acute toxicity: Mortality	Acute toxicity: ALD_{50} mg/kg
IIa	464	↑	↑	↑	↑	–	–	–	–	0	
	1000	↑	↑	↑	↑	–	–	–	–	0	>1000
	200	↑	↑	↑	↑	–	–	–	–	0	
IIb	464	↑	↑	↑	↑	+	–	–	–	0	
	1000	↑	↑	↑	↑	+	–	–	+	0	>1000
	200	↑	↑	↑	↑	–	–	–	–	0	
IIc	464	↑	↑	↑	↑	+	–	–	–	0	
	1000	↑	↑	↑	↑	+	–	–	–	0	>1000
	200	↑	↑	↑	↑	–	–	–	–	0	
IVa	464	↑	↑	↑	↑	–	–	–	–	0	
	1000	↑	↑	↑	↑	–	–	–	–	0	>1000
	200	↑	↑	↑	↑	–	–	–	–	0	
IVb	464	↑	↑	↑	↑	–	–	–	–	0	
	1000	↑	↑	↑	↑	–	–	–	–	0	>1000
	200	↑	↑	↑	↑	–	–	–	–	0	
IVc*	464	↓	↓	↓	↓	–	+	+	+	0	
	1000	↓↓	↓↓	↓↓	↓↓	–	++	+	–	100	681
	186.2	↓	↓	↓	↓	–	–	–	–	0	

SMA = Spontaneous motor activity.
↓ or ↑ = decrease or increase.
+ or ++ = mild or strong effect.
– = No effect.

CNS Activity :

Compound Nos. IIa, IIb, IIc, IVa and IVb in Table 1 and IVc [3-diethylaminoacetyl-2-(4'-fluorophenyl)indole] have been screened for CNS activity on different parameters in mice of either sex weighing between 18-25 gms. All the compounds were administered intraperitoneally (i.p.) as suspension in gum acacia.

1. *Acute Toxicity* : The compounds were administered to groups of mice in increasing doses[12]. The animals were observed for 24 hrs and the lethality after that time was used for determining the LD_{50} values. At least 3 dose levels were obtained between levels of 100% mortality and no mortality in each case.

The compounds are not toxic. Approximate LD_{50} is more than 1000 mg/kg in all cases except IVc. ALD_{50} for IVc is 681 mg/kg.

2. *Gross Effects :* The animals were observed for 2 hrs after drug administration for any evidence of CNS stimulation or depression or any autonomic effect by the method of Dhar *et al*[14]. This involved noting the effects on (i) spontaneous motor activity (ii) certain reflexes eg. righting, corneal and pinnal (iii) muscle tone (reduced and catalepsy) (iv) ataxia and writhing (v) eyes (pupils and ptosis) (vi) respiration, and (vii) observing them for the occurrence of tremors, convulsions, straub's tail, piloerection. Each effect was graded as mild(+) or strong(++).

SMA, respiration and reactivity increases in compound Nos. IIa, IIb, IIe, IVa and IVb, but decreases in IVc. Therefore, all compounds except IVc are stimulant. The results have been recorded in Table 2.

3. *Analgesic Activity :* This was tested by tail pinch method[15]. The compounds have been found devoid of analgesic activity.

4. *Anticonvulsant Activity :* This was tested by Supra Maximal Electroshock Seizure pattern[16]. The mice were fixed with electrode clamps on the ears. An electric current (48 mA, 0.2 sec.) was passed with a Techno Convulsometer and it induced tonic extension of hind limbs in 100% of untreated controls. The test compounds were administered i.p. to animals and half an hour later electroshock was given. The effective compounds protected electric shock.

Compound No. IVc has shown 20% anticonvulsant activity.

Acknowledgement

The authors wish to express their thanks to Prof. B. N. Dhawan, Deputy Director, Central Drug Research Institute, Lucknow, India, for providing necessary facilities for the evaluation of CNS activity and to Indian Council of Medical Research, New Delhi, India, for financing the project.

References

1. a. A. Cerletti, *Progr. Drug. Res.*, 1960, **2**, 227 ;
   b. V. Erspamer, *Progr. Drug. Res.*, 1961, **3**, 151 ;
   c. R. V. Heinzelman and J. Szmuszkovicz, *Progr. Drug. Res.*, 1964, **6**, 75.
2. C. A. Demerson, L. G. Humber, A. H. Philipp and R. R. Martel, *J. Med. Chem.*, 1976, **19**, 391.
3. V. Erspamer, *Science*, 1955, **121**, 369.
4. H. H. Keasling, R. E. Willette and J. Szmuszkovicz, *J. Med. Chem.*, 1964, **7**, 94.
5. R. Littell, G. R. Allen, Jr.-U. S., 1969, 3, 449, 363 ; *Chem. Abstr.*, 1969, **71**, 49764g.
6. Laboratoire d' Analyses et de Recherches Biologiques Mauvernay, Centre Europeen de Recherches Mauvernay (C. E. R. M.), Brit. 1, 116, 196 (1968) ; *Chem. Abstr.*, 1968, **69**, 87017g.
7. B. A. Whittle and E. H. P. Young, *J. Med. Chem.*, 1963, **6**, 378.
8. J. N. Delgado and E. I. Isaacson in 'Medicinal Chemistry' A. Burger, 3rd ed., Pt. II, Wiley-Interscience, New York, London, 1970, p. 1398.
9. J. G. Hirivakkanavar, S. Siddappa, C. H. Itagi and D. S. Patil, *Indian J. Chem.*, 1964, **2**, 352.
10. W. E. Noland, L. R. Smith and K. R. Rush, *J. Org. Chem.*, 1965, **30**, 3457.
11. K. C. Joshi, V. N. Pathak and P. Chand, *J. Prakt. Chemie*, 1978, **320**, 701.
12. K. C. Joshi, V. N. Pathak and P. Chand, *Indian J. Chem.*, 1978, **16B**, 933.
13. R. A. Turner, 'Screening Methods in Pharmacology' Academic Press, New York, 1965, p. 302.
14. M. L. Dhar, M. M. Dhar, B. N. Dhawan, B. N. Mehrotra and C. Ray, *Indian J. Expt. Biol.*, 1968, **6**, 232.
15. C. Bianchi and J. Franceschini, *Brit. J. Pharmacol. Chemotherap.*, 1954, **9**, 280.
16. E. Swinyard, *J. Amer. Pharm. Ass. Sci. Ed.*, 1949, **38**, 201.

NOTES

Complex Formation of Au(III) with Chromotropic Acid

R. C. SHARMA and M. S. BARARIA

Chemistry Department, Govt. College, Kota (Rajasthan), India

Manuscript received 4 April 1979, accepted 30 December 1979

CHROMOTROPIC acid (H_4A) figures prominently in the discussion of hydroxy carboxylic acids and provides two –OH groups for coordination. This has attracted the attention of many workers to explore the interaction of this acid with many metal ions[1-3]. A close examination of the existing literature reveals the absence of any study on Au(III)-chromotropic acid system.

Experimental

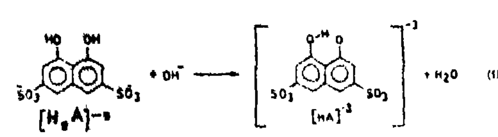
AnalaR (B.D.H) sodium hydroxide, gold chloride supplied by Johnson Mathey & Co., London and disodium salt of CTA (E. Merck) were used. A Cambridge *p*H meter was used to determine the H^+ concentration of the reaction mixtures.

Conductance measurements were carried out by a conductometer (WTW Leitfahigkeitsmesser, type IBR, made in Germany) with magic eye as a visual indicator.

The experimental procedure consisted of potentiometric and conductometric titrations of ligand in the absence and presence of gold chloride against standard alkali.

Results and Discussion

The appearance of inflection and breaks after the addition of one mole of alkali per mole of ligand (Fig. 1, Curve 1 & 1') correspond to the neutralisation of one of the phenolic –OH groups of CTA. There is no inflection and break observed for the second –OH, because of hydrogen bond formation[4]. The reaction may be represented as



When ligand is mixed with Au(III) solution in 1 : 1 ratio, there is observed a considerable lowering in the *p*H, due to complex formation. This mixture when titrated against standard alkali gave two inflections at m = 1 & m = 2 (Curve 2, Fig. 1). The first inflection corresponds to the neutralisation of $H(AuCl_3OH)$, the form in which aqueous solution of $AuCl_3$ exists[5]. The second inflection at m = 2 corresponds to the formation of a complex ion $(AuACl_2)^{-3}$. The reactions may be represented as :

$$H(AuCl_3OH)+OH^- \rightarrow (AuCl_3OH)^- + H_2O \quad \ldots (2)$$

$$(AuCl_3OH)^- + (H_2A)^{-2} + OH^- \rightarrow (AuACl_2)^{-3} + Cl^- + 2H_2O \quad \ldots (3)$$

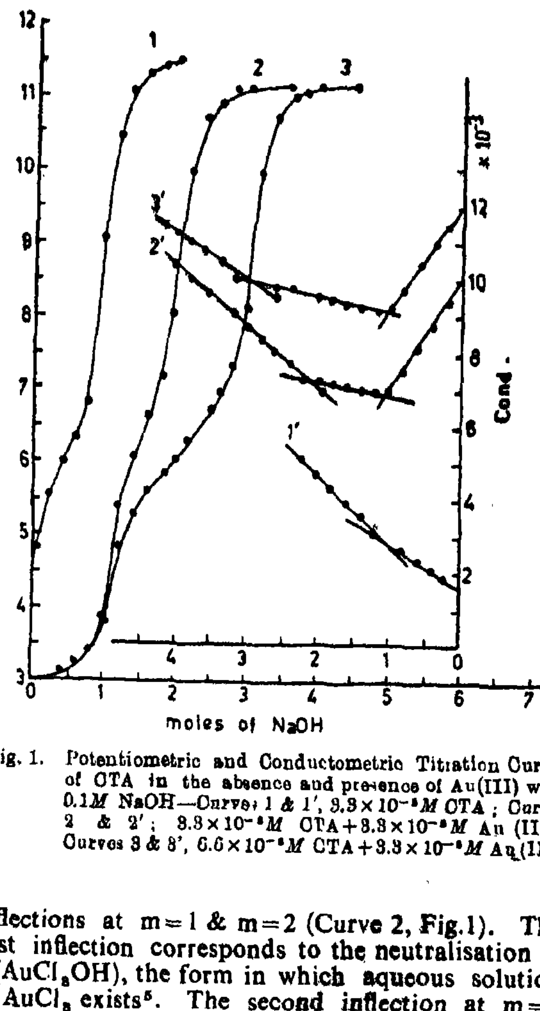


Fig. 1. Potentiometric and Conductometric Titration Curves of CTA in the absence and presence of Au(III) with 0.1*M* NaOH—Curves 1 & 1', 3.3×10^{-3}*M* CTA ; Curves 2 & 2' ; 3.3×10^{-3}*M* CTA + 3.3×10^{-3}*M* Au (III) ; Curves 3 & 3', 6.6×10^{-3}*M* CTA + 3.3×10^{-3}*M* Au(III).

Titration of 2 : 1 mixture of ligand and Au(III) solution against standard alkali indicates two inflections at m = 1 and m = 3 (Curve 3, Fig. 1). The first corresponds to the neutralisation of $H(AuCl_3OH)$ and the second corresponds to the formation of complex ion $(AuACl_2)^{-3}$. Anion $(HA)^{-3}$ is not neutralised owing to H-bond formation as shown

in equation 1. The reactions may be represented as :

$$H(AuCl_3OH)+OH^- \rightarrow (AuCl_3OH)^- + H_2O \quad \ldots (4)$$

$$2(H_2A)^{-2}+(AuCl_3OH)^- + 2OH^- \rightarrow (AuACl_2)^{-3} + H_2O + HA^{-2} + Cl^- \quad \ldots (5)$$

The formation of complex ion $(Au\ ACl_2)^{-3}$ is further confirmed by conductometric titrations. The breaks at m = 1 and m = 2 in the 1 : 1 mixture and at m = 1 and m = 3 in 2 : 1 ligand—Au(III) solution mixture confirm the formation of complex as shown by equations given above.

The present investigation clearly reveals the formation of 1 : 1 complex in *p*H range 7-10.

Acknowledgement

The authors are highly thankful to Dr. S. K. Verma, Principal, Shri K. P. Bhargave, Head of Chemistry Department, Govt. College, Kota for providing facilities for carrying out this work.

References

1. C. K. Sharma, V. D. Gupta and R. C. Mehrotra, *J. Indian Chem. Soc.*, 1973, **50**, 207.
2. R. Wake, H. Miyata and Tobik, *Bull. Chem. Soc. Japan*, 1968, **41**, 1952.
3. A. Banerjee and A. K. Dey, *J. Inorg. Nuclear Chem.*, 1968, **30**, 995.
4. R. Wake, H. Miyata and Tobik, *Bull. Chem. Soc. Japan*, 1968, **41**, 1952.
5. M. S. Kharasch and H. S. Inbell, *J. Amer. Chem. Soc.*, 1931, **53**, 2704.

Cu(II), Ni(II) and Co(III) Complexes of a Mixed Oxygen-Nitrogen Donor

S. Ghosh and T. K. Bandyopadhyay

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-700 032

Manuscript received 19 November 1979, accepted 25 December 1979

THE metal complexes of the tridentate O – N – N donors usually exhibit interesting magnetic, spectral and structural properties[1-3]. The strategic disposition of the donor sites in many of such ligands forces the metal ions to demerise or polymerise, leading to metal complexes where antiferromagnetic interaction becomes their special characteristic. In this preliminary communication, we report the ligational behaviour of benzoylhydrazone of biacetylmonoxime (LH_2) towards Co(III), Ni(II) and Cu(II) ions in both its keto and enol forms.

In an alcoholic medium of *p*H 4-5, the ligand behaves as a tridentate neutral donor and forms 1 : 1 type Cu(II) complexes. With Ni(II) only 1 : 2 type chelates have been isolated. In the case of the Co(III) complex, the initially used Co(II) salt is found to be oxidised to Co(III) and a complex of the formula $Co(LH)_2H_2O$ is isolated. In a medium of *p*H 6-8, where the enol-form predominates, neutral Co(III), Ni(II) and Cu(II) chelates, corresponding to a metal : ligand ratio of 1 : 1, have been synthesised in the case of Cu(II) and Ni(II) and 1 : 2 in the case of Co(III). The analytical data and room temperature magnetic moment values of the complexes are given in Table 1. The room temperature magnetic moment of all the Cu(II) complexes of the keto form of the ligand lie within the range of 1.77-1.81 B.M. and is indicative of either a square-planar or a distorted octahedral stereochemistry[4]. For the Ni(II) complexes, the magnetic moment values lie in the range of 2.91-3.00 B.M. The Co(III) complexes of the keto and the enol forms of the ligand are diamagnetic. The Ni(II) complex of the enol form of the ligand is also diamagnetic ; whereas, the Cu(II) complex shows subnormal magnetic moment value (1.00 B.M.) at room temperature indicating a strong spin-spin interaction within this chelate molecule, probably existing in a dimeric state.

TABLE 1

Complex	Colour	Analysis %			μ_{eff} B.M. 300°K
		Metal	Nitrogen	Anion	
$Co(LH)_2.H_2O$	Orange	8.18 (8.31)	16.90 (17.08)	—	Diamagnetic
$Co(LH)(L)$	Chocolate red	11.84 (11.92)	17.12 (17.00)	—	Diamagnetic
$Ni(LH_2)_2Cl_2.2H_2O$	Yellowish grey	9.58 (9.73)	13.80 (13.91)	11.80 (11.74)	2.98
$Ni(LH_2)_2Br_2.2H_2O$	Greenish grey	8.55 (8.47)	11.98 (12.12)	22.97 (23.07)	3.00
$Ni(LH_2)_2(NO_3)_2.2H_2O$	Pale yellow	9.00 (8.93)	16.95 (17.05)	—	2.91
$Ni(L)$	Brown red	21.16 (21.23)	15.14 (15.23)	—	Diamagnetic
$Cu(LH_2)Cl_2.H_2O$	Yellowish green	16.97 (17.10)	11.45 (11.30)	19.14 (19.00)	1.77
$Cu(LH_2)(NO_3)_2.H_2O$	Ultramarin blue	15.00 (14.96)	16.29 (16.48)	—	1.81
$Cu(L)$	Blackish green	22.51 (22.64)	15.00 (14.92)	—	1.00

* Figures in the parenthesis indicate the calculated values.

A comparison of the i.r. spectra of the ligand and the metal complexes in the keto form reveals that the broad band at 3320-3280 cm^{-1}, originally present in the ligand and assigned to the superimposed stretching vibrations of the –NH and the oxime –OH groups[5], has not been distinguished ; instead, there appears a broad and unsymmetrical absorption band around 3500-3200 cm^{-1}, which might be due to the stretching vibration of the coordinated or lattice water molecules overlapping the –NH and –OH stretches. A striking modification observed is that, the band at 1640 cm^{-1}, assigned as

the amide I band, is always shifted to a lower frequency by 15-40 cm^{-1} in the metal complexes, indicating the participation of the C=O group in coordination. Also, a positive shift of 20-65 cm^{-1} of the N–O stretch (1015 cm^{-1} in the ligand) in the chelated species is diagonistic of the oxime nitrogen coordination[6]. The C=N (azomethine) stretching frequency at 1590 cm^{-1} in the free ligand is found to be shifted to a lower frequency by 5-15 cm^{-1} in the complexes, suggesting its involvement in coordination. Regarding the complexes of the enol form of the ligand, which do not contain any water molecule, no identifiable absorption band in the region 3600-3200 cm^{-1} are present pointing to the absence of the –OH as well as the –NH groups. The strong amide I band at 1640 cm^{-1} is absent in all these complexes indicating the enolisation of the keto group and its participation in complexation in the enolate form. The N–O stretching frequency in all the complexes of the enol form has been observed at a higher frequency than is present in the original ligand. Cryomagnetic study of the Cu(II) complex of the enol form of the ligand is in progress and will be reported in near future.

References

1. W. E. HATFIELD and R. WHYMAN, "Transition Metal Chemistry", 1969, **5**, 47.
2. D. J. HODGSON, "Progress in Inorganic Chemistry", 1975, **19**, 1.
3. J. A. BERTRAND and P. G. ELLER, *Inorg Chem.*, 1974, **9**, 18, 928.
4. B. N. FIGGIS and C. M. HARRIES, *J. Chem. Soc.*, 1959, 855.
5. L. J. BELLAMY, 'The Infrared Spectrum of Complex Molecules", Chapman and Hall, London, 1975.
6. K. BURGER, I. RUFF and F. RUFF, *J. Inorg. Nuclear Chem.*, 1965, **27**, 179.

Nickel(II) Mixed Chelates Containing Two Bidentate Monobasic Hydroxyaldehyde (or Ketone) and a Bidentate (NN) Heterocycle

R. L. DUTTA and ANJANA BHATTACHARYA

Department of Chemistry, The University of Burdwan, Burdwan-713 104, West Bengal

Manuscript received 6 November 1979, accepted 20 December 1979

We have recently described[1,2] a series of pseudooctahedral nickel(II) mixed chelates containing a dibasic tridentate (ONO) Schiff base like salicylideneamino acid, one dipyridyl (or *o*-phenanthroline) and a molecule of water. The most useful method of synthesis of these mixed chelates involved a template reaction on *bis*(salicylaldehydato) dipyridyl nickel(II) and related complexes by the desired amino acids. Only a passing reference[3] to *bis*(3-nitrosalicylaldehydato) dipyridyl nickel(II) is available in the literature. We report in this note several nickel(II) mixed chelates containing two hydroxy aldehydes (or ketones) and one dipyridyl (or *o*-phenanthroline) with a fond hope that these mixed chelates may serve as useful precursors in forcing novel template reactions with chosen amines or amino acids. The following abbreviations have been used :

SalH = salicylaldehyde ; 5-Cl-salH = 5-chlorosalicylaldehyde ; 5, 6-benzosalH = 5, 6-benzosalicylaldehyde ; hacH = 2-hydroxyacetophenone ; dipy = dipyridyl and *o*-phen = *o*-phenanthroline.

Experimental

Bis(salicylaldehydato) diaquo nickel(II)[4] and other similar complexes were synthesised by published procedures.

Bis(salicylaldehydato) dipyridyl/o-phenanthroline nickel(II) :

Bis(salicylaldehydato) diaquo nickel(II) (0.002 mol) in alcohol (50 ml) was allowed to reflux with the heterocylic base (0.002 mol) for fifteen minutes. The green solution was filtered hot, concentrated to 10 ml, scratched and cooled in a refrigerator overnight. The green crystals were collected, dissolved in minimum volume of refluxing chloroform, filtered and cooled in ice. Finally the crystals were dried in air.

Bis(5-chlorosalicylaldehydato) dipyridyl/o-phenanthroline nickel(II) :

The chloroform solution obtained as above was concentrated to 2-3 ml. To this solution 5 ml alcohol was added with stirring and then left in a refrigerator overnight. Yellowish green crystals were collected and dried in air.

The remaining compounds were obtained by following the above procedures with or without some slight variation in the volume of solvent etc. The characterisation data are given in Table 1.

Results and Discussion

The magnetic moments (Table 2) lie in the range 3.14-3.24 B.M. being consistent with pseudooctahedral stereochemistry[5]. Their non-electrolytic nature[6] in methanol rules out any alternative ionic formulation such as $[Ni(sal)(dipy)_2]^+ [Ni(sal)_3]^-$. Nujol mull spectrum of $[Ni(dipy)(sal)_2]$ reveals two bands at ~10.2 kK (ν_1) and ~16.7 kK (ν_2) (Table 2). The absorption peaks are somewhat broad, thus indicating considerable distortion from octahedral geometry[7]. ν_1 and ν_2 are assigned as the transitions : $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ in O_h symmetry. ν_3 transitions could not be located with

TABLE 1—CHARACTERISATION DATA OF NICKEL(II) MIXED CHELATES (DRIED AT 120°C)

Chelates	Colour	Ni (%)		N(%)	
		Found	Calc.	Found	Calc.
[Ni(dipy)(sal)$_2$]	Green	12.6	12.8	6.2	6.1
[Ni(o-phen)(sal)$_2$]	Yellowish green	12.3	12.2	5.4	5.8
[Ni(dipy)(5-Cl-sal)$_2$]	Green	10.9	11.2	5.1	5.3
[Ni(o-phen)(5-Cl-sal)$_2$]	Yellowish green	10.8	10.7	5.1	5.1
[Ni(dipy)(5,6-benzosal)$_2$]	Light green	10.3	10.5	5.1	5.0
[Ni(o-phen)(5,6-benzosal)$_2$]	Brownish green	9.9	10.1	4.7	4.8
[Ni(dipy)(hac)$_2$]	Green	11.9	12.1	5.5	5.8
[Ni(o-phen)(hac)$_2$]	Yellowish green	11.6	11.5	5.3	5.5

Some of the air dried hydrated compounds were analysed for carbon, hydrogen (at C.D.R.I., Lucknow) and lattice water with satisfactory results.

TABLE 2—MAGNETIC MOMENT, CONDUCTIVITY AND ELECTRONIC SPECTRA OF NICKEL(II) MIXED CHELATES

Chelates	Magnetic moment (B.M.)	Conductivity in methanol (ohms^{-1}cm^{2}mole^{-1})	$\nu_1(\epsilon) = 10Dq$, kK	$\nu_2(\epsilon)$ kK	ν_2/ν_1
[Ni(dipy)(sal)$_2$]H$_2$O	3.19	2	10.20^a	16.7^a	1.64
[Ni(o-phen)(sal)$_2$]1.5H$_2$O	3.20	1	10.21(12.9)^b	16.66(24.2)^b	1.63
[Ni(dipy)(5-Cl-sal)$_2$]H$_2$O	3.19	1	10.21(9.3)^b	16.66(13.9)^b	1.63
[Ni(o-phen)(5-Cl-sal)$_2$]1.5H$_2$O	3.24	1	10.21(11.0)^b	16.66(20.8)^b	1.63
[Ni(dipy)(5,6-benzosal)$_2$]	3.17	2	10.60^a	17.20^a	1.28
[Ni(dipy)(hac)$_2$]1.5H$_2$O	3.20	1	—	16.94(7.2)^c	—

a = nujol mull ; b = chloroform ; c = ethanol.

certainty because of the high absorption of the heterocyclic donors. The spin-forbidden transition $^3A_{2g}(F) \rightarrow {}^1E_g$ could be detected in solution spectra in the region 11.3-13.2 kK (ϵ 3.0-8.5). The $\nu_2 : \nu_1$ ratios of the mixed chelates are around 1.62 indicating the pseudooctahedral nature of the chelates[8]. The 10 Dq ($= \nu_1$) values are consistent with the 10 Dq values of other [NiN$_2$O$_4$] chromophores (e.g. [Ni(tmen)(tfa)$_2$][9] : 10 Dq = 9.8 kK ; tmen = N, N,-N^1, N^1-tetramethyl ethylenediamine and tfa = trifluoroacetylacetonate ion).

The infrared spectrum of [Ni(dipy)(sal)$_2$] registers band at 1613 ($\nu_{C=O}$)[10], 1580 cm^{-1} (ν_{C-C})[11] and 740 cm^{-1} (ν_{dipy}). The $\nu_{C=O}$ band of [Ni(H$_2$O)$_2$-(sal)$_2$] appears at 1640 cm^{-1} and a typical dipyridyl band of [Ni(OH$_2$)Cl (dipy)$_2$]Cl.2H$_2$O shows up at 740 cm^{-1}. Thus we are convinced that in these mixed chelates we have both the hydroxyaldehyde and the heterocyclic donors coordinated to nickel(II).

Acknowledgement

We thank CSIR for financial assistance.

References

1. R. L. DUTTA and A. BHATTACHARYA, *J. Indian Chem. Soc.*, 1975, **52**, 668.
2. R. L. DUTTA and A. BHATTACHARYA, *J. Inorg. Nuclear Chem.* (in press).
3. Y. MUTO, *Bull. Chem. Soc. Japan*, 1960, **33**, 604.
4. A. D. DAMODARAN, F. M. ICHAPORIA and G. S. RAO, *J. Indian Chem. Soc.*, 1968, **45**, 690.
5. F. A. COTTON and G. WILKINSON, Advanced Inorganic Chemistry, 3rd Edition, Interscience, New York (1972).
6. W. J. GEARY, *Coord. Chem. Revs*, 1971, **7**, 81.
7. J. R. MILLER, Advances in Inorganic and Radiochemistry, (Ed.) H. J. EMELEUS and A. G. SHARPE, Academic Press, 1962, Vol. 4, p. 148.
8. L. SACCONI, 'Transition Metal Chemistry', (Ed.) R. L. CARLIN, Mercel Dekker, New York, 1968, Vol. 4, p. 214.
9. Y. FUKUDA and K. SONE, *J. Inorg. Nuclear Chem.*, 1975, **37**, 455.
10. R. H. BALUNDGI and A. CHAKRAVORTY, *Inorg. Chem.*, 1973, **12**, 981.
11. A. R. KATRITZKY, A. R. HANDS and R. A. JONES, *J. Chem. Soc.*, 1958, 3165.

Mixed Ligand Complexes. Part IX. Methioninato *bis*(biguanide) Cobalt(III) Salts

R. L. DUTTA and ANJANA BHATTACHARYA

Department of Chemistry, The University of Burdwan, Burdwan-713 104

Manuscript received 6 November 1979, accepted 20 December 1979

METHIONINE(I) is a flexidentate ligand being capable of chelating as a tridentate (SNO) and bidentate(SN) and (NO) donors. Preparation and properties of the mixed chelate [Co(meth)(BigH)$_2$]$^{2+}$ (meth H = methionine) were undertaken to ascertain the donor sites. Attempts to synthesise

the mixed chelate containing cysteine and biguanide ended in failure.

$$CH_3-S-CH_2-CH_2-\underset{\displaystyle NH_2}{\underset{|}{CH}}-COOH$$

(I)

Experimental

Biguanide acid sulphate[1] and *cis*-diammine *bis* (biguanide) cobalt(III) base[2] were prepared by published procedures. Aminoacidato *bis*(biguanide) cobalt(III) compounds[3] were also obtained by procedures developed in this laboratory (α-alanH= alanine ; valinH = valine ; leucH = leucine).

dl-Methioninato bis(biguanide) cobalt(III) iodide :

Cis-diammine *bis*(biguanide) cobalt(III) base (0.003 mol) in water (20 ml) was allowed to react with *dl*-methionine (0.003 mol) on a steam bath for forty minutes. After ammonia evolution had ceased the solution was filtered and neutralised with HCl (1 : 3) followed by the addition of KI (~1 gm). The solution was then allowed to stand overnight at room temperature. The separated red-violet crystals were further purified from hot water. (Found : Co, 8.8 ; N, 22.8 ; I, 37.1 ; H_2O, 2.7%. Calc. for [Co(*dl*-meth) $(BigH)_2$] $I_2.H_2O$: Co, 8.7 ; N, 22.6 ; I, 37.3 ; H_2O, 2.6%).

dl-Methioninato bis(biguanide) cobalt(III) sulphate :

The above reaction mixture was neutralised with 10% H_2SO_4. The solution was concentrated to 10 ml and on cooling in a refrigerator reddish violet crystals separated. These were triturated with a little hot water, filtered and washed with alcohol. Found : Co, 11.8 ; N, 30.7 ; SO_4, 19.0%. Calc. for [Co(*dl*-meth)$(BigH)_2$]SO_4 : Co, 11.7 ; N, 30.5 ; SO_4, 19.0%.

l-Methioninato bis(biguanide) cobalt(III) sulphate :

l-Methionine and *cis*-diammine *bis*(biguanide) cobalt(III) base were reacted as described above and the solution was neutralised with H_2SO_4. The sparingly soluble sulphate salt was recrystallised from a large volume of hot water. Found : Co, 11.2 ; N, 29.3 ; SO_4, 18.7 ; H_2O, 3.5%. Calc. for [Co(*l*-meth) $(BigH)_2$] $SO_4.H_2O$: Co, 11.3 ; N, 29.5 ; SO_4, 18.4 ; H_2O, 3.4%.

Elemental analyses were done by following standard methods. Equivalent weight was determined with the aid of H^+ form cationexchanger (IR-120) column[3]. Conductance was determined with a Philips Bridge at 0.001*M*. Spectra of aqueous solutions were run in 1 cm cell over the range 320-600 nm in a Hilger Uvispek Spectrophotometer.

Results and Discussion

Molar conductance of [Co(*dl*-meth) $BigH)_2$] $I_2.H_2O$ in water was found to be 211 $ohms^{-1}$ cm^2 $mole^{-1}$ being in the expected range of bi-univalent electrolytes[4]. Its equivalent weight (339) was close to the required value (340). The electronic spectrum[5] of this complex was extremely close to those of [Co-(*dl*-α-alan)$(BigH)_2]^{2+}$, [Co(*dl*-valin)$(BigH)_2]^{2+}$, [Co (*l*-leuc)$(BigH)_2]^{2+}$ in respect of spectral profile, band positions and molar extinction coefficients :

	$^1A_{1g}\to{}^1T_{1g}(\epsilon_{max})$	$^1A_{1g}\to{}^1T_{2g}(\epsilon_{max})$
[Co(*dl*-meth)$(BigH)_2]^{2+}$	20.41(165) (kK)	27.90(214) (kK)
[Co(*dl*-α-alan)$(BigH)_2]^{2+}$	20.41(155)	27.78(187)
[Co(*dl*-valin)$(BigH)_2]^{2+}$	20.62(161)	27.78(199)
[Co(*l*-leuc)$(BigH)_2]^{2+}$	20.41(144)	27.78(78)

The properties of [Co(*l*-meth)$(BigH)_2]^{2+}$ are also comparable to those of [Co(*dl*-meth)$(BigH)_2]^{2+}$. It is thus clear that the above mixed chelates have [CoN_5O] chromophore i.e. methionine functions as a bidentate NO donor. The sulphur end of methionine remains unattached to cobalt(III). In the mixed chelate $[Co(cys)(en)_2]^+$ ($cysH_2$ = cysteine ; en = ethylenediamine) the cysteinate ligand has been shown to be attached to cobalt(III) as an SN bidentate donor[6]. The $^1A_{1g}\to{}^1T_{1g}$ transition appears at a lower energy (16.7 kK).

Acknowledgement

We thank CSIR for financial assistance to one of us (A.B.).

References

1. D. Karipides and W. C. Fernelius, 'Inorganic Synthesis', Ed. J. Kleinberg, McGraw Hill Book Co. Inc., New York, 1963, Vol. 7, p. 56.
2. R. L. Dutta and S. Sarkar, *J. Indian Chem. Soc*. 1967, **44**, 853.
3. R. L. Dutta and A. Bhattacharya, *J. Indian Chem. Soc*., 1975, **52**, 1002.
4. W. J. Geary, *Coord. Chem. Revs*., 1971, **7**, 81.
5. A. B. P. Lever, 'Inorganic Electronic Spectroscopy', Elsevier Publishing Co., Amsterdam, 1968.
6. V. M. Kothari and D. H. Busch, *Inorg. Chem*., 1969, **8**, 2276.

Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) Complexes of Acrylamide

A. SAMANTARAY, P. K. PANDA and B. K. MOHAPATRA

Department of Chemistry, Ravenshaw College, Cuttack-753 003, Orissa

Manuscript received 16 November 1979, accepted 20 December 1979

AMIDES and lactams have invoked lot of interest as ligands in recent years, since in addition to the carbonyl group, these molecules possess an amine group as a potential donor site. Further, these

complexes are being widely used in polymerization processes. With transition metal ions only compounds have been reported that contain oxygen co-ordinated amides and lactams. This aroused our interest to study a number of lactams and amides as ligand. In earlier communication, we have described[1-3] complexes of lactams, nicotinamide and dicyandiamide with some divalent metal ions. Though a few complexes of acrylamide with metal salts containing non-coordinating anions have been reported[4-5], these reports are controversial so far as the bonding site (donor atom) is concerned. It was therefore thought worthwhile to study the complexes of acrylamide with some divalent metal ions.

Experimental

All the chemicals used were of AnalaR grade. Absolute ethanol solution of the divalent metal salts were reacted with ethanolic solution of acrylamide in 1 : 6 and 1 : 8 proportions. Resulting solutions were refluxed for one hour and kept standing for one or two days when compounds crystallized out. These were filtered under suction, washed with ethanol and ether and dried in vacuum. The metal and halogen or thiocyanate were analysed by standard methods. Conductance was measured in M/1000 acetone solution of complexes using Toshiniwal conductance bridge. Magnetic susceptibility measurements were made on solid specimens by Gouy's method at room temperature. Infrared spectra were recorded from Perkin-Elmer-337 and Beckman IR-12 spectrophotometers. Electronic spectra were measured with M/100 (chloroform + amide) solution by Hilgerwatt Uvispeck spectrophotometer. All the relevant analytical data are recorded in Table 1.

Results and Discussion

All the complexes reported have the general composition MX_2L_2 where $X = Cl^-$, Br^- or SCN^- and L = acrylamide except the two pink cobalt complexes which have the formula $CoBr_2L_4$ and $Co(SCN)_2L_4$. Other cobalt(II) complexes are deep blue in colour, nickel(II) complexes are green, copper(II) complexes are either green or yellow, manganese(II) complexes are light pink, zinc and cadmium complexes are white. All the compounds are soluble in acetone, in which medium the molar conductance values are in the range of 5-12 mhos cm^2 indicating non-electrolytic nature. Magnetic moment of blue cobalt(II) complexes indicate a tetrahedral configuration where as the pink complexes have higher moments suggestive of a spin free octahedral configuration. Nickel(II), copper(II) and manganese(II) complexes have moments in the range of 2.9-3.0, 1.75-1.82 and 5.9-5.92 B.M. respectively.

Infrared spectra of acrylamide show bands at 3350, 3180, 1680, 1620 and 1440 cm^{-1} region assignable[6] to $\nu_{as}(N-H)$, $\nu_s(N-H)$, $\nu(C=O)$ (amide-I), $\delta(NH_2)$ (amide-II) and $\nu(C-N)$ respectively. In the complexes the band positions due to $\nu(N-H)$ remain almost unaltered whereas $\nu(C=O)$ is observed ~1660 and $\nu(C-N)$ ~1460 indicating that acrylamide in bonded to the metal ions through the carbonyl oxygen atom. This has been further substantiated by observation[7] of $\nu(M-O)$ ~420-450 cm^{-1} region in the far infrared spectra of complexes. In case of thiocyanato complexes $\nu(C\equiv N)$ is observed ~2100 cm^{-1} suggesting the presence of N-bonded terminal thiocyanato group on the basis of earlier observations[8].

Visible electronic spectra of cobalt(II) complexes classify them into two distinct categories

TABLE 1—ANALYTICAL AND SPECTRAL DATA OF ACRYLAMIDE (L) COMPLEXES

Compounds	M.P. (°C)	Λ M (mhos. cm^2)	μ_{eff} (B.M.)	% Metal		% Halogen or thiocyanate		Electronic spectra ν_{max} in k.k. (ε)
				Found	Calcd.	Found	Calcd.	
1. $CoCl_2L_2$	230	5.8	4.5	21.24	21.6	25.72	26.07	16.5(950), 8.2(200)
2. $CoBr_2L_2$	Above 250	6.5	4.6	16.02	16.27	44.03	44.3	16.3(940), 8.8(200)
3. $CoBr_2L_4$	245	7.4	4.9	11.31	11.67	31.55	31.78	18.8(35), 8.2(20)
4. $Co(SCN)_2L_4$	212	8.2	5.0	12.65	12.83	25.04	25.32	18.9(33), 8.1(20)
5. $NiCl_2L_2$	Above 250	9.1	2.9	21.32	21.6	25.87	26.09	8.5(6), 13.3(6), 24.1(14)
6. $NiBr_2L_2$	Above 250	10.8	3.1	16.05	16.27	44.11	44.31	8.8(7), 13.5(7), 24.3(15)
7. $Ni(SCN)_2L_2$	237	11.5	3.0	18.14	18.51	36.24	36.62	9.1(7), 13.5(7), 24.5(14)
8. $CuCl_2L_2$	Above 250	8.4	1.8	22.74	22.97	25.26	25.64	14 8(35)
9. $CuBr_2L_2$	Above 250	6.8	1.82	17.03	17.38	43.38	43.72	15.1(38)
10. $Cu(SCN)_2L_2$	Above 250	7.5	1.75	19.51	19.74	35.91	36.07	17.8(42)
11. $MnCl_2L_2$	188	11.2	5.9	20.11	20.49	25.14	26.49	27.5(.35), 24.6(.2)
12. $MnBr_2L_2$	208	12.0	5.92	15.14	15.39	44 55	44.78	27.2(.3), 24.5(.2)
13. $ZnCl_2L_2$	112	8.2	—	23.01	23.48	25.03	25.47	
14. $Zn(SCN)_2L_2$	237	10.5	—	19.88	20.2	35.66	35.86	
15. $CdCl_2L_2$	165	8.8	—	34 28	34.52	21.58	21.81	
16. $CdBr_2L_2$	178	9.2	—	26.85	27.13	25.14	25.49	

COL_2X_2 type of complexes show two absorption bands ~16.5 (950) and ~8.5 (200) k.k. region attributable to $^4A_2 \rightarrow ^4T_{1g}$ (P) and $^4A_2 \rightarrow ^4T_1$ (F) transitions respectively suggesting a tetrahedral stereochemistry of these complexes supported by their magnetic moment data. Complexes of the composition CoX_2L_4 also show two absorption bands ~18. (35) and 8.2 (20) k.k. region assignable to $^4T_{1g} \rightarrow ^4T_{1g}$(P) and $^4T_{1g} \rightarrow ^4T_{2g}$ (F) transitions respectively. On the basis of the spectral bands and their magnetic moments a spin free octahedral configuration is indicated for these complexes supported by earlier observation[6]. All the nickel(II) complexes give rise to three absorption bands ~8.5-9.1 (6), 13.3-13.5 (6) and 24.1-24.5 (14) k.k. regions due to $^3A_{2g}(F) \rightarrow ^3T_{2g}(F), \rightarrow ^3T_{1g}(F)$ and $\rightarrow ^3T_{1g}(P)$ transitions respectively and a possible spin free octahedral stereochemistry is suggested[10] for these complexes. Copper(II) halide complexes show one broad band ~14.8-15.1 (38) k.k. region and the thiocyanate complex shows one band at 17.8 (42) k.k. region. Presumably the halide complexes have a distorted octahedral configuration[11] whereas the thiocyanate complex is planar. Two bands are observed in case of manganese(II) complexes ~27.5 and 24.6 k.k. regions suggesting[12] an octahedral environment about the metal ion. On the basis of analysis, conductance and infrared spectral studies zinc and cadmium complexes have a possible tetrahedral geometry.

Acknowledgement

Thanks are due to U.G.C., New Delhi for financial assistance and Research & Development Department, Hindustan Photo Films Ltd., Ootacamond for recording the I. R. spectra.

References

1. C. D. RAO and B. K. MOHAPATRA, *J. Inorg. Nuclear Chem.* (London), 1977, **39**, 689.
2. C. D. RAO, S. GURU and B. K. MOHAPATRA, *J. Indian Chem. Soc.*, 1976, **53**, 1240.
3. P. K. PANDA and B. K. MOHAPATRA, *J. Inorg. Nuclear Chem.* (London), (In Press).
4. B. G. RAMSEY and J. G. GRASSELI, *Inorg. Chim. Acta*, 1969, **3**, 503.
5. J. REEDIJIK, *Inorg. Chim. Acta*, 1971, **5**, 687.
6. R. M. SILVERSTEIN and G. C. BASSLER, "Spectrometric Identification of Inorganic Compounds"—(John Wiley, New York), 1967.
7. J. R. FERRARO, "Low Frequency Vibrations of Inorganic and Co-ordination Compounds", (Plenum Press), 1971.
8. A. TRAMER, *J. Chim. Phys.*, 1962, **59**, 232.
9. D. P. GRADDON and E. C. WATTON, *Aust. J. Chem.*, 1965, **18**, 507.
10. B. N. FIGGIS, "Introduction to Ligand Fields", (Wiley Eastern, New Delhi), 1976.
11. A. B. P. LEVER "Inorganic Electronic Spectroscopy" (Elsevier, Amsterdam), 1968.
12. S. K. MADAN and J. A. STURR, *J. Inorg. Nuclear Chem.*, 1967, **29**, 1669.

Unstable Chromium(III) Chlorate

M. R. UDUPA

Department of Chemistry, Indian Institute of Technology, Madras-600 036, India

Manuscript received 29 October 1979, accepted 22 December 1979

PERCHLORATES and chlorates are powerful oxidizing agents and the thermal decomposition of intimate mixtures of chromium(III) oxide and $LiClO_4$, $TlClO_4$, $KClO_3$ and $KClO_4$ resulted in the formation of metal dichromates. Chromium(III) perchlorate hexahydrate on thermolysis[5] gives chromium(VI) oxide and chromyl chloride. In this context, it was thought interesting to study the thermal behaviour of chromium(III) chlorate and to identify the decomposition products in order to find out whether Cr(III) is oxidized into Cr(VI) by the chlorate moiety. No information is available in the literature about the preparation and existence of this compound. In this note is reported the attempted method of isolation of $Cr(ClO_3)_3$ and its immediate oxidation to Cr(VI).

Experimental

10 m moles (6.622 g) of $Cr_2(SO_4)_3.15H_2O$ are dissolved in 100 ml water and to which is added a solution containing 30 m moles (9.667 g) of $Ba(ClO_3)_2.H_2O$ in 100 ml water. The contents are stirred for 15 min and the precipitated $BaSO_4$ is filtered. The filtrate containing $Cr(ClO_3)_3$ solution is checked for Cr(III) content by iodometry after oxidizing Cr(III) with potassium peroxydisulphate[6]. A known amount of the $Cr(ClO_3)_3$ solution was taken in a petri dish and was evaporated on a water bath. Blue colour of the solution persisted till the complete evaporation of water and suddenly the thick liquid turned into a red mass. The electronic spectrum was recorded on a Carl Zeiss DMR 21 recording spectrometer and the infrared spectrum was taken on a Perkin-Elmer 257 spectrometer in nujol mull. The X-ray powder photograph was taken using CuKα radiation and Debye-Scherrer camera of diameter 11.46 cm.

Results and Discussion

The red mass obtained, is found to be hygroscopic and its electronic spectrum in water exhibited absorptions at 23.0, 28.8 and 39.0 kK, which are the characteristic of $[CrO_3(OH)]^-$ species[7]. The infrared spectrum showed absorption bands at (cm^{-1}) 975s and 850w, b which are due[8] to CrO_3. Further, the X-ray powder patterns of the solid showed the most intense lines at (Å) 4.23, 3.40 and 3.33 which correspond[9] to CrO_3. Further confirmation of the solid was achieved by chemical analysis. Known amount of $Cr(ClO_3)_3$ solution was taken in an all-glass apparatus, with a provision to collect the liberated

gases, and heated to 100°. The evolved gases during the concentration and conversion to CrO_3 was collected in a flask containing water. If Cr(III) oxidized as gaseous CrO_2Cl_2, it is hydrolyzed and Cr(VI) is determined iodometrically after boiling off the dissolved chlorine in the solution. Cr(IV) is also determined in the residual red mass. The analytical results are given in Table 1, which suggest

Table 1—Data on Analysis of Chromium

$(Cr^{3+}+3ClO_3^-)$ taken (m mole)	Found (m mo'e) CrO_2Cl_2	CrO_3	Molar ratio CrO_3/CrO_2Cl
0.10	0.032	0.066	2.06
0.15	0.051	0.102	2.00
0.25	0.085	0.172	2.02

that 2/3 of Cr(III) is oxidized into CrO_3 and the remaining one-third to CrO_2Cl_2. The reaction scheme is given as

$$(Cr^{3+}+3ClO_3^-) \rightarrow 2/3\ CrO_3 + 1/3\ CrO_2Cl_2 + 7/6\ Cl_2 + 19/6\ O_2$$

Slow evaporation of chromium(III) chlorate solution at room temperature, either keeping at open atmosphere or in a desiccator also resulted in the formation of CrO_3 after several days. Cr(VI) also formed in solution on boiling the acidified $Cr(ClO_3)_3$ solution. The fact that Cr(VI) formed after the removal of water from the chromium chlorate solution and only by boiling the acidified solution indicates that $Cr(ClO_3)_3$ is probably a low melting compound. However, all the attempted methods to isolate the solid, met with no success.

References

1. A. Burcat, I. Pelly and M. Steinberg, *J. Inorg. Nuclear Chem.*, 1968, **30** 41.
2. M. R. Udupa and G. K. Ramachandra, *Thermochim. Acta*, 1974, **9**, 427.
3. M. R. Udupa, *Thermochim. Acta*, 1975, **12**, 165.
4. M. R. Udupa, *Thermochim. Acta*, 1975, '3, 349.
5. M. R. Udupa, *Thermochim. Acta*, 1975, **13**, 246.
6. A. I. Vogel, 'A Textbook of Quantitative Inorganic Analysis', Longman Inc., 1978.
7. C. K. Jorgensen, 'Absorption Spectra and Chemical Bonding in Complexes', Addition-Wesely, Massachussets, 1962.
8. N. T. McDevit and W. L. Baun, *Spectrochim. Acta*, 1964, **20**, 799.
9. 'Inorganic Index to the Powder Diffraction File', JCPDS, 1971.

Ligational Behaviour of o-Aminobenzoylhydrazine towards some Transition Metal Ions

S. Ghosh* and T. K. Bandyopadhyay

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-700 032

Manuscript received 19 November 1979, accepted 25 December 1979

Acidhydrazides and their derivatives have received considerable attention because of their potentiality as versatile coordinating agents[1,2] as well as their antibacterial activity[3-5]. Extensive search of literature showed that no work has been done on the metal chelates of *o*-aminobenzoylhydrazine (LH), a potential tridentate ligand. We have also observed that this ligand molecule is capable of inhibiting the growth of some strains of tuberculosis mycobacteria[6]. In the present communication, we wish to make a preliminary report on the chelating behaviour of *o*-aminobenzoylhydrazine (LH) towards Co(II), Ni(II) and Cu(II) ions. With Cu(II) salts, both mono- and *bis*-chelates have been isolated; whereas, the Co(II) and Ni(II) salts forms only 1 : 2 type complexes. In all these cases the ligand behaved as a neutral one. All the metal complexes have been prepared by reacting the metal salts with the ligand in warm aqueous-ethanol in 1 : 2 proportion, when microcrystalline complexes separated slowly. For the preparation of 1 : 1 type Cu(II) complexes, 1 : 1 molar ratio of the metal salt and the ligand was used. The analytical data and magnetic moment values of some of the representative complexes are given in Table 1.

The effective magnetic moment values for the complexes, $Cu(LH)_2X_2.4H_2O$ ($X=NO_3$, $\frac{1}{2}SO_4^{-2}$), fall in the range of distorted octahedral Cu(II) complexes[7]. On the other hand, the Cu(II) complexes of the formula $Cu(LH)X_2.4H_2O$ ($X=Cl^-$, Br^-, NO_3^-, $\frac{1}{2}SO_4^{-2}$), exhibit subnormal magnetic moment values. The Ni(II) and Co(II) complexes show paramagnetism corresponding to two and three unpaired electrons respectively, in an octahedral environment[8,9]. The electronic spectral data for all the complexes are also indicative of octahedral disposition of the donor sites around the metal ions.

The ligand molecule possess three potential donor sites namely, the carbonyl oxygen, the hydrazinic $-NH_2$ and the ring NH_2 groups. The i.r. spectrum of the ligand in KBr exhibits bands at 3420 cm^{-1} and 3250 cm^{-1}. The first one may be assigned to the stretching vibration of the ring $-NH_2$[10] and the second one to the superimposed stretching vibrations of $-NH$ bands of the hydrazinic amino and imino groups. The lowering of the band at 3250 cm^{-1} by 10-50 cm^{-1} in the metal complexes is suggestive of hydrazinic $-NH_2-$ coordination to the metal ions. The ligand shows a strong absorption band at 1655 cm^{-1} (amide I band), which

*For communication.

TABLE 1

Complex	Colour	Analysis% Metal	Nitrogen	Anion	μ_{eff} B.M. 300°K
$Co(LH)_2Cl_2.4H_2O$	Light Pink	11.52 (11.69)	16.80 (16.67)	13.95 (14.07)	5.00
$Co(LH)_2Br_2.4H_2O$	Flesh Coloured	9.86 (9.94)	14.06 (14.17)	26.62 (26.96)	4.80
$Co(LH)_2(NO_3)_2.4H_2O$	Pinkish White	10.48 (10.58)	19.97 (20.10)	—	4.77
$Co(LH)_2SO_4.4H_2O$	Pinkish White	11.05 (11.14)	15.69 (15.88)	18.20 (18.14)	4.83
$Ni(LH)_2Cl_2.4H_2O$	Bluish Grey	11.58 (11.65)	16.75 (16.67)	13.95 (14.07)	4.00
$Ni(LH)_2Br_2.4H_2O$	Bluish Grey	9.78 (9.90)	13.99 (14.17)	26.78 (26.97)	3.01
$Ni(LH)_2(NO_3)_2.4H_2O$	Bluish Grey	10.48 (10.54)	20.00 (20.11)	—	2.98
$Ni(LH)_2SO_4.4H_2O$	Sky blue	10.98 (11.10)	15.95 (15.88)	18.05 (18.15)	2.91
$Cu(LH)Cl_2.4H_2O$	Light Green	17.60 (17.75)	11.58 (11.75)	19.61 (19.84)	1.37
$Cu(LH)Br_2.4H_2O$	Dirty Green	14.07 (14.21)	9.52 (9.41)	35.53 (35.81)	1.48
$Cu(LH)(NO_3)_2.4H_2O$	Light blue	15.33 (15.45)	17.16 (17.05)	—	1.44
$Cu(LH)SO_4.4H_2O$	Greenish blue	16.48 (16.59)	10.78 (10.98)	24.87 (25.10)	1.43
$Cu(LH)_2(NO_3)_2.4H_2O$	Light Green	11.20 (11.30)	19.84 (19.94)	—	1.80
$Cu(LH)_2SO_4.4H_2O$	Light Green	11.77 (11.89)	15.58 (15.74)	16.78 (17.03)	1.83

* Figures in the parenthesis represent the calculated values.

suffers a depression of 20-55 cm^{-1} in the chelated species indicating the participation of the carbonyl group in bonding to the metal ion through its oxygen atom. As is observed here, bonding from the carbonyl oxygen and the terminal $-NH_2$ of the acid hydrazides is a well established fact[1,2].

In view of the subnormal magnetic moment values of the 1 : 1 Cu(II) complexes, the following dimeric formulation (Fig. 1.), in which the carbonyl group act as a bridge between two Cu(II) centres, is proposed :

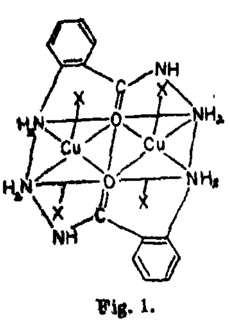


Fig. 1.

Cryomagnetic studies on the 1 : 1 Cu(II) complexes are being done and will be reported soon.

References

1. R. M. ISSA, M. F. EL-SHAZLY and M. F. ISKANDER, *Z. Anorg. Allg. Chem.*, 1967, **354**, 90.
2. YU. YA. KHARITONOV, R. I. MACKKHOSHVILI, P. V. GOGORISHVILI and KARKASHVILI, *Zh. Neorg. Khim.*, 1972, **17(4)**, 1051 ; *Zh. Neorg. Khim*, 1972, **17(4)**, 1059.
3. J. C. CYMERMAN, D. WILLIS, S. D. RUBBO and J. EDGAR, *Nature*, 1955, **176**, 34.
4. H. H. FOX, J. T. GIBAS and A. MOTCHANE, *J. Org. Chem.*, 1956, **21**, 356.
5. NG. PH. HO BUU, *J. Chem. Soc.*, 1953, 1358.
6. T. K. BANDYOPADHYAY, Ph.D. Dissertation of Calcutta University, 1979.
7. B. N. FIGGIS and C. M. HARRIES, *J. Chem. Soc.*, 1959, 855.
8. N. S. GILL and R. S. NYHOLM, *J. Chem. Soc.*, 1959, 3997.
9. B. N. FIGGIS, *Nature*, 1958, **182**, 1568.
10. L. J. BELLAMY, "The Infrared Spectrum of Complex Molecules", Chapman and Hall, London, 1975.

A Study of Vanadyl(IV) Complex of Fluorescein—Thermal Studies of Amine Adducts. Part-VII.

LEELA PARDESHI and R. A. BHOBE*

Department of Chemistry, Marathwada University, Aurangabad, Maharashtra, India

Manuscript received 27 November 1979, accepted 25 December 1979

DETAILED studies on complexes of fluorescein including that of vanadyl[5], have already been reported[1-5]. The vanadyl ion having a strong and dominant axial field and four ligand moieties

* Senior author to whom all correspondence should be addressed.

flat in the equatorial plane can accommodate[4], trans to vanadyl oxygen, the solvent molecules of NH_3, $-CH_3$, $-C_2H_5$ and $C_4H_9NH_2$ to give an octahedral complex/adduct. Thermal dissociation of such ammonia and ammine adducts of vanadylfluorescein complex give ΔH, ΔF and ΔS values (K cals/mole/degree) as 11.85, 3.24, 28.90 for NH_3 adduct, 14.70, 2.89, 39.60 for CH_3NH_2 adduct, 15.68, 3.19, 41.75 for $C_2H_5NH_2$ adduct and 21.40, 3.20, 54.50 for $C_4H_9NH_2$ adduct.

The vanadyl complex of fluorescein is a violet black paramagnetic entity whose structure has been reported by us[5]. It was interesting to observe that this complex formed adducts with NH_3 (dark violet), with CH_3NH_2 (brownish violet), with $C_2H_5NH_2$ (dirty brown) and with $C_4H_9NH_2$ (dark brownish black). Pressure studies indicated that thermal dissociation of these adducts are smooth and measurable.

Preparation and Analysis :

The liquid amines formed adducts with VO $(FLCN)_4$ easily when the latter was suspended in ethanol and when a slight stoichiometric excess amine was mixed at ~30°. The NH_3 adduct was formed when gaseous NH_3 was passed for twenty-four hours through finely powdered VO $(FLCN)_4$. In all the cases, the adducts formed were flushed thoroughly with pure nitrogen gas. The analysis was carried out with the usual microtechniques and are given in Table 1 (V = Vanadium metal).

TABLE 1

Adduct of	%elements (obsd) V	C	H	N	%elements (calcd) V	C	H	N
Ammonia	4.11	68.03	3.44	—	3.86	68.19	3.34	—
Methyl amine	3.66	68.98	3.39	45.06	3.58	68.30	3.45	45.16
Ethyl amine	3.51	68.46	3.59	30.96	3.56	68.40	3.56	31.11
Butyl amine	3.40	68.79	3.82	15.94	3.48	68.74	3.76	16.09

Experimental

The adducts were carefully heated with an automatic thermoregulator. Pressures generated were transmitted to Hg in capillary and the heights recorded with the help of a cathetometer, recording 0.001 cm accurately. The results were reproducible with fresh samples of the adduct, and also reversible which is the prerequisite for thermodynamic calculations given below.

Results and Discussion

The values of T (°K) vs pressures (mm) are not given in tabular form but are depicted as plots of $10^3/T$ vs log P in Fig. 1 and the slopes and ΔH (K cals) values are set out in Table 2.

TABLE 2—VALUES OF SLOPES FROM THE PLOTS OF log P vs $10^3/T$ AND ΔH VALUES

Adduct with :	Slope × 10^{-3}	ΔH (K cals/mole)
Ammonia	5.99	11.85
Methyl amine	7.50	14.70
Ethyl amine	7.92	15.68
Butyl amine	10.75	21.40

The free energy data ΔF and the entropies ΔS (at 25°) were calculated by standard Eyring equations. The relevant values are shown below (Table 3).

TABLE 3 · ΔF AND ΔS ALONG WITH ΔH VALUES (TABLE 2) FOR THE AMMONIA AND AMINE ADDUCTS OF $VO(FLCN)_4$

Thermodynamic quantities (K cals/mole)	Ammonia adduct	CH_3NH_2 adduct	$C_2H_5NH_2$ adduct	$C_4H_9NH_2$ adduct
ΔH	11.85	14.70	15.68	21.40
ΔF	3.24	2.89	3.19	3.20
ΔS	28.92	39.60	41.75	54.50

A similar work on gaseous boron trimethyl adducts with NH_3 and amines[6] give comparable results in that ΔH values for this adduct range from 3.75 to 23.48 K cals/mole and ΔS from 39.90 for the ammonia adduct to 44.70 for the butyl adduct, in both the cases, showing an increasing trend as the number of carbon atoms increase. A slight deviation in the case of ammonia adduct may be attributed to changes in the rotational entropy losses of the ligand when NH_3 molecule gets co-ordinated within the crystal lattice in the present case as against the gaseous molecules of boron trimethyl ammonia adduct[7].

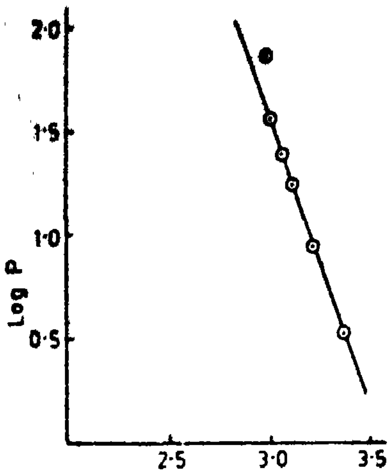
$$(\Delta S\ VO(FLCN)_4.NH_3 = 28.92\ ;\ \Delta S\ (CH_3)_3.B.NH_3 = 39.90).$$

Since log P vs 1/T plots (Figs. 1 to 4) are fairly on a straight line, it may be assumed that enthalpy changes are almost constant and ΔS varies inversely with temperature. That means, at the expense of heat absorbed, the vapour pressure of the ligand (FLCN) gets raised. Table 4 below gives an idea of net changes that take place between temperatures 25° to 60°.

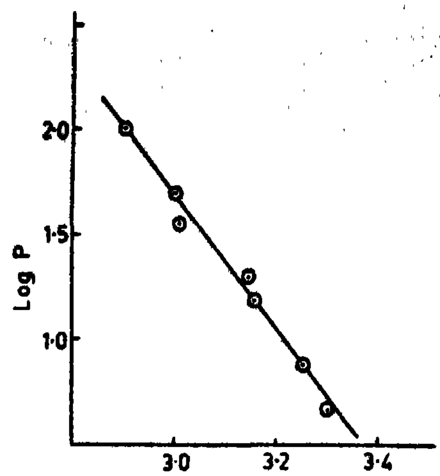
TABLE 4—NET CHANGES (cals/mole) IN THE AMINE ADDUCTS OF $VO(FLCN)_4$

Amine adduct	NH_3	CH_3NH_2	$C_2H_5NH_2$	$C_4H_9NH_2$
ΔS at 25°C	28.90	39.60	41.75	54.50
ΔS at 60°C	29.10	34.40	42.05	59.60
Net changes	−0.20	1.20	−2.30	−5.10

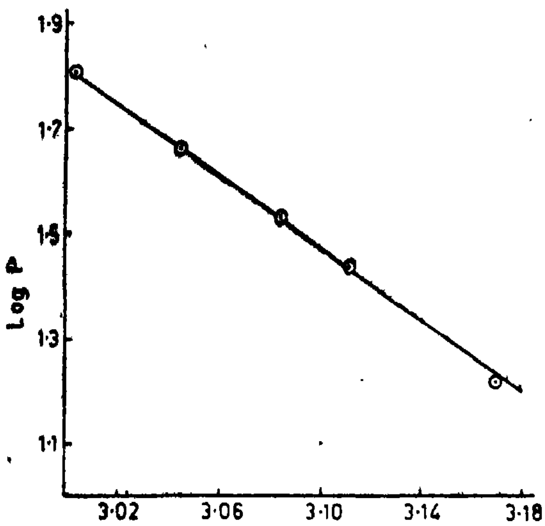
C_v value for NH_3 is taken as 6.57 cal/mole/degree[8]. It seems that for 35° change (25° to 60°), the changes in vapour pressure of the NH_3 adduct correspond to change of entropy effect −0.20, which



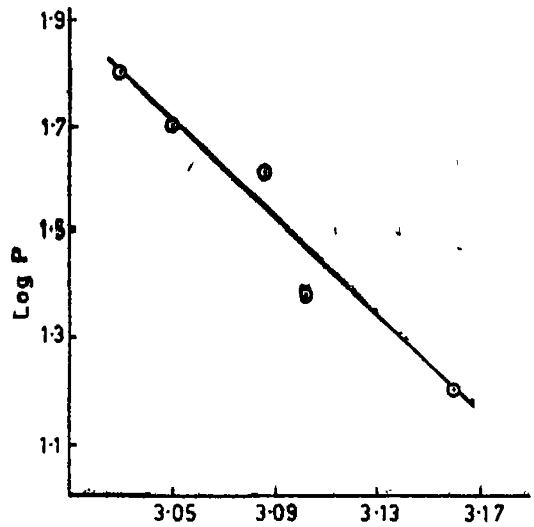
$^1/_T \times 10^3$ Fig 1



$^1/_T \times 10^3$ Fig. 2



$^1/_T \times 10^3$ Fig. 3



$^1/_T \times 10^3$ Fig. 4

may be ascribed to transfer of NH_3 or amine molecule from the solid to the gaseous state. The translational entropies ΔS (trans) can be easily calculated[9] and the absolute values ΔS (abs) by standard equations[10].

These are listed in Table 5.

TABLE 5—ΔS(trans), ΔS(abs) AND ΔS(obsd) VALUES FOR $VO(FLCN)_4$ ADDUCTS WITH NH_3 AND AMINES'

Adduct	ΔS(trans)	ΔS(abs)	ΔS(obsd)
NH_3	34.58	45.50	28.90
CH_3NH_2	36.84	57.96	39.60
$C_2H_5NH_2$	37.70	69.06	41.75
$C_4H_9NH_2$	39.20	84.42	54.50

The values in Table 5 clearly indicates that heavier the amine, greater is the contribution to translational entropy. May be, factors such as hydrogen bonding are playing a dominant role in the distribution of entropies.

In the Table 6, competitive factor between NH_3 and other amines has been brought out. It gives one a rough idea about the relative structural effects when a ligand A_1 replaces A_2 as

$$VO(FLCN)_4.A_2+A_1 \rightleftharpoons VO(FLCN)_4+A_2+A_1$$

It will be observed from the data (Table 6) that when ammonia as a ligand is replaced by $C_4H_9NH_2$ or when CH_3NH_2 by $C_4H_9NH_2$, the entropy changes are exceptionally large thus indicating that the size of the replacing ligand plays a vital role.

TABLE 6—COMPETITIVE FACTORS INVOLVED IN REPLACEMENT OF LIGAND A_2 BY A_1

A_2	A_1	ΔF_{298} cals/mole	ΔH_{298} cals/mole	ΔS_{298} cals/mole/degree
NH_3	CH_3NH_2	+850	−2850	−10.70
NH_3	$C_2H_5NH_2$	+300	−3850	−12.85
NH_3	$C_4H_9NH_2$	+ 40	−9550	−25.60
CH_3NH_2	$C_2H_5NH_2$	−300	− 980	− 2.00
CH_3NH_2	$C_4H_9NH_2$	−210	−6700	−14.90
$C_2H_5NH_2$	$C_4H_9NH_2$	− 10	−5700	+12.75

VO_2^{+2} will have a square pyramidical configuration. It is expected that this will assume either a regular or distorted octahedron structure when the ammonia or amine molecules are added to it. Search of literature[11-13] reveals a distorted octahedron structure for a vanadyl ion. With ammonia adduct, free energy changes seem to be miximum and decreases somewhat when the length of carbon chain in the amine added increases. The entropy effects are in reverse order. The order of the entropy units for butyl-amine adduct predicts that a spontaneous replacement in this case is rather difficult. There are approximations involved in assuming a regular octahedron structure for VO^{2+} complex. In fact, crystal field theory predicts that the change from a regular octahedron to the square pyramidical structure is associated with an increased stability. The data presented in Table 6 merely shows that variations in symmetry of the complex molecule may take place and a preferred configuration will be assumed by the complex molecule when the ligand A gets attached to it loosely.

Acknowledgement

Our thanks are due to Dr. K. A. Thakar, Professor and Head, Department of Chemistry, Marathwada University, Aurangabad, Maharashtra, India, for extending to L. G. P. all the facilities for Post doctoral work and for continued support.

References

1. R. A. BHOBE, *J. Indian Chem. Soc.*, 1973, **50**, 442.
2. R. A. BHOBE, *J. Indian Chem. Soc.*, 1974, **51**, 846.
3. R. A. BHOBE, *J. Indian Chem. Soc.*, 1975, **52**, 390.
4. R. A. BHOBE, *J. Indian Chem. Soc.*, 1977, **54**, 344.
5. R. A. BHOBE, *J. Indian Chem. Soc.*, 1977, **54**, 347.
6. BROWN *et al.*, "Determination of Organic Structures by Physical Methods" ed. Braude and Nachod, Academic Press, Inc. New York, N. Y. 1955, ch. 14.
7. A. KNOP and S. BRUBAKER, *J. Inorg. Nuclear Chem.*, 1959, **8**, 9.
8. "Physical Chemistry" by Danniels and Alberty, John Wiley and Sons, Inc. New York, 1955, p. 105.
9. GLASSTONE'S "Thermodynamics for Chemists", D. Van Nostrand Co. Inc. Princeton, New Jersey, 1964 (East-West Student Edition).
10. "Chemical Thermodynamics" by Klotz, Prentice Hall, Inc., New York, N. Y., 1950, p. 172-177.
11. R. L. CARLIN and F. A. WALKER, *J. Amer. Chem. Soc.*, 1965, **87**, 2128.
12. J. SELBIN, L. H. HOLMES JR. and S. P. McGLYNN, *J. Inorg. Nuclear Chem.*, 1963, **25**, 1359.
13. D. N. SATYANARAYANA and C. C. PATEL, *J. Inorg. Nuclear Chem.*, 1965, **27**, 297.

Extraction and Complexometric Determination of Copper in Brass using Dimethyl Glyoxime as an Indicator

MONOJIT BAKSHI GUPTA

Central Laboratory, Indian Standards Institution, New Delhi-110 002, (India)

Manuscript received 26 November 1979, accepted 30 December 1979

DIMETHYL Glyoxime[1] has already been used as an indicator for the complexometric titration of copper by the present author. The use of dimethyl glyoxime in analytical chemistry is well known. It has been used for the determination[2] of Ni, Pd(II), Pt(II), Iron(II) and Bismuth.

This paper reports the use of dimethyl glyoxime as an indicator for the complexometric titration of copper in brass or bronze samples.

Experimental

Reagents and Solutions :

(i) EDTA solution : a stock solution of 0.1*M* EDTA was prepared by dissolving 37.23 gm of EDTA (Sodium salt) in 1 litre of distilled water.

(ii) Dimethyl Glyoxime (2%) : Prepared by dissolving in absolute alcohol.

(iii) EDTA solution (4%) : Prepared in distilled water.

(iv) Sodium diethyl dithio carbamates (1%) : The solution is prepared in distilled water.

(v) Ammonium Hydroxide : Dilute (2%)

(vi) Tartaric Acid : Solid

(vii) Ethyl acetate : B.D.H/E. MERCK

(viii) Silver nitrate solution : 2% in distilled water.

Procedure : 0.5 gm drillings of the brass or bronze sample is dissolved in dilute nitric acid (1 : 2) and tartaric acid (about 0.2 gm) in a beaker and transferred in a 250 ml volumetric flask and the solution is diluted upto the mark. 250 ml of the solution is drawn in a separating funnel. 15 ml of EDTA solution (4%) is added to it, the *p*H is maintained at 8.5 with ammonium hydroxide. Now

copper is precipitated with 50 ml of sodium diethyl dithio carbamate[3] solution (1%) and the ppt. is extracted with ethyl acetate. All copper is removed in one extraction. The ethyl acetate layer is washed and copper from the organic phase is displaced (15 ml) with silver nitrate[4] solution. Finally, the solution is strongly diluted and made weakly basic with ammonium hydroxide and then the copper is titrated with EDTA using 10 ml of dmethyl glyoxime (1%) as an indicator from red to blue end point.

Results and Discussion

A number of brass and bronze samples are tested by this method against the electrolysis method and iodometric method and their results are indicated in Table 1, which are in good agreement with one another.

TABLE 1

Particulars of Samples	Iodometric Method	Cu by Electrolysis	Cu by New Method*
No. 1	70.02	70.04	70.11
No. 2	70.18	70.25	70.20
No. 3	68.48	68.56	68.50
No. 4	70.52	70.58	70.62
No. 5	67.70	67.77	67.74

* Average of 3 results.

Determination of copper by electrolysis though accurate is expensive and time consuming. On the other hand, the new method is cheaper, takes much less time and the results are reproducible as well.

Acknowledgement

The author is grateful to Dr. S. Ghosh, Director, Central Laboratory, ISI, New Delhi for his keen interest and permission to publish this paper.

References

1. M. BAKSHI GUPTA and A. DATTA, *J. Instt. Chemists* (India), Sept. 1979 (In the press).
2. Flagg, "Organic Reagents", Interscience Publishers, INC, New York, 1948, p. 14?.
3. A. I. VOGEL, 'A Text Book of Quantitative Inorganic Analysis'. The English Language Book Society and Longmans Green and Co. Ltd. 1961, p. 901.
4. FRANK J. WELCHER, The analytical uses of EDTA, D. Van Nostrand Co., New York, 1958, p. 247.

Analytical Applications of 5-Hydroxy-1, 4-Naphthoquinone (Juglone)

S. S. SAWHNEY and B. M. L. BHATIA

Chemistry Department, D. A. V. (P.G.) College, Dehradun (U.P.)

Manuscript received 9 November 1979, accepted 20 December 1979

THE present note extends the application of juglone as a pH indicator[1] in the determination of glycine and hippuric acid, and deals with its use as a metal ion indicator in the estimation of nickel ion in solution complexometrically with hippuric acid as a titrant at 6.8 pH.

In the titration of hippuric acid (N/50 and N/100) with NaOH (N/46.30 and N/96), juglone with pH range 7.8-9.9 and colour change : yellow to violet, was found more suitable than phenolphthalein, methyl-red and lapachol[2]. Standard deviation as low as 0.05 could be achieved in the case of juglone. Relative errors in different case are :

Indicator	Relative Error (%)	
Analyte :	N/50	N/100
Titrant :	N/46.30	N/96
Juglone	0.21	0.41
Phenolphthalein	0.75	2.50
Methyl-red	3.45	4.58
Lapachol	2.15	5.41

In the estimation of glycine, juglone as a pH indicator in the place of phenophthalein, employing sorenson formula in titration method, with relative error as 0.02% is quantitative in nature. Standard deviation as low as 0.02 could be achieved.

Juglone as Metal Ion Indicator :

Nickel-juglone complex with metal ligand molar ratio of 1 : 2 is less stable than nickel-hippuric acid complex having metal to ligand combining ratio as 1 : 2. With progressive complexation of nickel ion by hippuric acid at 6.8 pH, nickel ion is ultimately displaced from nickel-juglone complex (red) to leave free juglone (yellow). Juglone exhibits acid-base behaviour in the pH range 7.8-9.9 in which it exhibits violet colour. It is yellow below 7.8 pH. Nickel forms red complex[3] with juglone at 6.8 pH.

Under the experimental conditions, juglone as a metal ion indicator with relative error as 0.6% appears to be suitable in the estimation of nickel ion complexometrically. E.D.T.A. titration yielded far better results. Standard deviation as low as 0.3 could be achieved. Ions like Co^{2+}, Cu^{2+}, Mn^{2+}, Al^{3+}, Fe^{3+}, interfered.

Procedure :

Dilute 5 ml (0.1 *M*) nickel ion solution to 10 ml with distilled water. Add 4 ml of buffer solution (6.8 *p*H) and 1 ml (0.02*M*) indicator. Titrate with (0.02*M*) hippuric acid until colour change from red to yellow. Blank was also run for better results.

References

1. S. S. SAWHNEY and N. C. TREHAN, *Indian J. Chem.*, 1976, **14A**, 295.
2. S. S. SAWHNEY and N. VOHRA, *J. Indian Chem. Soc.*, 1977, **54**, 408.
3. Y. NAGASE and U. MATSUMOTO, *Yakugaku Zasshi.*, 1961, **81**, 622 ; *Chem. Abs.*, 1961, **55**, 21692e.

Direct Estimation of Zinc in Complex Materials

DHARAM PRAKASH, CHANDRA SHEKHAR

and

SURESH CHANDRA

Chemical Laboratory, Directorate of Geology and Mining, 2 Way Road, Lucknow

Manuscript received 19 November 1979, accepted 20 December 1979

ZINC belongs to the more common trace elements. Its average concentration in the lighosphere is in the order of 60-70 p.p.m. It mostly occurs as the sulfide, sphalerite, ZnS, but the carbonate smithsonite $ZnCO_3$ and the silicate willemite $Zn_2(SiO_4)$ are also common zinc minerals. The occurrence of zinc in silicate rocks was examined by Sandell and Goldich who found that the amounts of zinc present in rocks of the plutonic and volcanic series could be related to the sum of the magnesium and ferrous iron, and also to the manganese content. Rader has also shown that the zinc content of basaltic rocks can be related to the total iron content. In metallurgical products particularly in the non-ferrous field zinc is often encountered and its analysis called for, except where it is one of the principal constituents. as in brass (Zn, Cu) German Silver (Zn, Cu, Ni) and in die casting alloys (Zn, Cu, Al) where it is commonly reported by difference. Granulated zinc is a necessary substance in the chemical laboratory. Its resistance to rusting makes zinc valuable as a protective coating on iron surfaces (galvanized iron). Considerable quantities of zinc are used as anodes in electrical batteries. The ZnO is used as a pigment and chemical in rubber goods, including automobile tyres and extensively as a paint pigment. It is used in glazes, in enamels, as an ointment, as dusting powder etc. The chloride is used as a preservative of wood. The sulfide is a valuable white pigment, with barium sulphate it forms lithopone. Recently zinc has been shown to be necessary to the growth of plants, certain chemical glasswares contain from 3-11% zinc. Zinc determination should not be made in these wares.

The quantitative estimation of zinc in a complex material, where it is associated with, Cu, Pb, Al, Fe, Mg, Ca, Cd etc. is a tedious process. The gravimetric methods are quite lengthy, because the separation of each group is required before reaching the IV group (Zn, Ni, Co, etc. comes in fourth group) and also during the precipitation of zinc with diammonium hydrogen phosphate magnesium interferes. In the volumetric analysis zinc can be titrated with EDTA using Eriochrome Black T at *p*H 10 but in the presence of Mg this method proved futile.

Zinc at *p*H 6 forms coloured complex with xylenol orange (red complex). When it is titrated with standard EDTA, the colour change at the equivalence point is from red to yellow. This method has successfully been applied for the estimation of zinc present in rock and minerals where it is generally associated with several elements viz. Cu, Pb, Al, Fe, Mg, Ca and Cd etc.

In the proposed method Pb has been removed as $PbSO_4$ and filtered off alongwith silica. Iron has also been removed as iron-hydroxide by precipitating it with NaOH, copper and aluminium is complexed with sodium thiosulphate and sodium fluoride respectively and zinc is titrated directly with standard 0.01*M* EDTA at *p*H 6 (which was maintained using hexamine) using 0.5% xylenol orange as indicator. The colour change at the end point is from red to yellow. Magnesium and calcium do not interfere at *p*H 6.

Reagents :

1-EDTA : 0.01*M* – 3.7225 gms of EDTA was weighed and dissolved in one litre of distilled water.

2-Sodium thiosulphate – 10% soln. 10 gms of sodium thiosulphate was dissolved in 100 ml distilled water.

3-Sodium fluoride 5% solution – 5 gms sodium fluoride was dissolved in 100 ml distilled water.

4-Hexamine – It is used as buffer to maintain *p*H 6.

5-Xylenol orange 0.5% (0.5 gms) of the reagent was weighed, dissolved in little alcohol and was made upto 100 ml by distilled water.

Experimental

Several samples of zinc were weighed. The samples were decomposed by 1 : 2 HNO_3 and

evaporated nearly to dryness. To this 2-3 ml of conc. H_2SO_4 was added, and the solution was evaporated on a hot plate to fumes of sulphur trioxide in order to expel nitric acid. The presence of even a small quantity of NO_3 ions increases the solubility of the lead sulphate. The residual liquid is treated with 50 ml of distilled water and the insoluble lead sulphate alongwith silica is filtered of after digesting the solution. The filtrate so obtained is made upto 100 ml in volumetric flasks. 20 ml of the solution was taken out by a pipette in a beaker. To this solution 50 ml of distilled water was added, and the solution was heated. To the hot solution 5% solution of NaOH was added, dropwise to precipitate iron as $Fe(OH)_3$, aluminium goes into solution as sodium aluminate, Cu and Zn also remain in the solution $Fe(OH)_3$ was filtered off. The filterate was then acidified with dil HCl. To this solution 2 ml of 10% sodium thiosulphate was added to complex copper ions and 2 ml of 5% sodium fluoride was added to complex aluminium ions, 2-3 drops of xylenol orange was added, then solid hexamine was added with agitation until the colour of the solution becomes red (*p*H 6). The solution was titrated with 0.01*M* EDTA until the colour changes from red to yellow. The reading was noted and the percentage of zinc in the samples was calculated.

By Atomic Absorption Spectrophotometer :

For the estimation of zinc by Atomic Absorption Spectrophotometer a standard calibration graph was prepared. The absorbances were noted against known concentration of zinc. The unknown samples of zinc were then run through the instrument and the absorbances were noted. By interpolating the values in the standard graph the percentage of Zn was determined.

The results obtained by this method have been compared successfully with those obtained by instrumental method i.e. the samples were run on Atomic Absorption Spectrophotometer and the results are given in the Table :

	Percentage of Zn	
	By A.A.S.	Proposed method
1.	1.10	1.05
2.	0.50	0.42
3.	10.00	9.75
4.	8.20	8.10
5.	6.00	5.60
6.	0.30	0.12
7.	00.60	0.37
8.	1.20	0.99
9.	5.20	4.97
10.	4.36	4.06

Results and Discussion

Xylenol orange forms complex with zinc at *p*H 6 which was maintained by Hexaine (Hexamethylene tetramine) but the Zn-EDTA complex is more stable than dye-Zn complex and at the equivalence point all the zinc ions are complexed with EDTA and the xylenol orange dye remains in the solution which is yellow in colour. Copper and aluminium do not interfere as they have already been complexed with sodium thiosulphate and sodium fluoride respectively. Magnesium and calcium also do not interfere as they do not form complex at *p*H 6.

References

1. E. B. SANDELL and S. S. GOLDICH, *J. Geol.*, 1943, **51**, 99 and 167.
2. L. F. RADER, W. C. SWADLEY, H. H. LIPP and C. HUFFMAN, JR. U. S. Geol. Surv. Prof. Paper Leoo B. p. B 487, 1960.
3. A. I. VOGEL, A Text Book of Quantitative Inorganic Analysis, The English Language Book Society & Longman Green & Co. Ltd., 1962.
4. W. W. SCOTT and H. F. Furman, Standard Method of Chemical Analysis. The Technical Press Ltd., 1956.
5. W. F. HILLEBRAND and G. E. F. LUNDELL, Applied Inorganic Analysis, John Willey and Sons, INC New York, Chapman & Hall Limited London, 1953.
6. F. J. WELCHER, The Analytical Use of Ethylene Diamine Tetraacetic Acid. D. Van. Nostrand Company Inc. Princeton, New Jersey, New York, U.S.A., 1961.

Photometric Study of Uranyl-Terramycin Complex*

P. B. SANKARA REDDY**, A. V. R. REDDY

and

S. BRAHMAJI RAO

Department of Chemistry, SVU Autonomous Post-Graduate Centre, Anantapur-515 003

Manuscript received 20 November 1979, accepted 22 December 1979

THE spectrophotometric investigation of uranyl-terramycin complex in solution has been studied photometrically at *p*H 1.3. The composition of the complex is established by Job's and Slope ratio methods as 1 : 1. The stability constant calculated from the data obtained in Job's method is 1.9×10^8. Beer's law is obeyed.

A survey of literature has revealed that much work has not been done on the "Metal complexes of antibiotics" particularly of terramycin. Metal complexes of streptomycin have been studied by Foye and Lange[1] and Zahn and Eisenbrandt[2]. Uranyl-streptomycin complex has been recently studied spectrophotometrically by Agarwal *et al*[3]. The spectrophotometric investigation of uranyl-terramycin complex has been carried out and results are communicated here.

*Presented at the Annual Convention of Chemists, held at Kurukshetra, September 23-27, 1979.

** Department of Chemistry, Government College (Men), Cuddapah-516 004, A. P., India.

Experimental

All the chemicals employed are of analytical grade. Spectrophotometric measurements were made with Elico Spectrocol model CL-23 (India) and pH measurements with Elico Degital pH Meter model LI-120. The reagent solution was prepared in 1,4-dioxane. All the other solutions were prepared in double distilled water.

Absorbance of the reagent and the reaction mixture consisting of uranyl ion and the reagent is measured in the pH range 1-4.5 in the wavelength range 400 nm to 650 nm. The absorbance difference for the reaction mixture (metal ion+excess reagent) and the reagent was maximum at 425 nm. Hence further studies were carried out at this wavelength.

Effect of pH :

To the buffered solution (pH 1.3 to 4.5) metal solution and the reagent solution were added so that the overall concentration of each component is $1.0\times10^{-3}M$. The absorbance for each reaction mixture is measured against the buffer solution as the blank. The absorbance of the mixture increased while that of the reagent decreased with increase in pH. However, at pH's higher than 2.5 the solution became turbid slowly and hence further studies are restricted to pH 1.3.

Obedience of Beer's law :

The absorbance of the reaction mixture varied linearly with the concentration of uranium in presence of excess of reagent. This shows that small amounts of uranium can be estimated colorimetrically with the reagent.

Composition and Stability constant :

Slope ratio method and Job's method indicated that the composition of the complex is 1 : 1. The stability of the complex is calculated from the data obtained in the Job's method and is 1.9×10^{8}.

Acknowledgement

The authors express their gratitude to the Director, SVU Autonomous Post-Graduate Centre, Anantapur for providing necessary facilities. One of the authors (PBSR) expresses his gratitude to UGC, New Delhi for the award of Teacher Fellowship under FIP and to the Director of Higher Education, Government of Andhra Pradesh for deputation.

References

1. W. O. Foye and W. E. Lange, *J. Am. Pharm. Assoc.*, 1955, 44, 261.
2. G. Zahn and Eisenbrandt, *Pharmasie*, 1964, 19, 407.
3. J. K. Agarwal *et al*, *Proc. Ind. Acad. Sci.*, 1975, 82, 65.

Quantitative Separation of Co^{++} or Cd^{++} or Cu^{++} from Ca^{++} and PO_4^{3-} and Their Complexometric Determination

P. P. MAHAPATRA*, H. MISHRA and N. S. CHICKERUR

Department of Chemistry, Khallikote College, Berhampur (Ganjam)-760 001, India

Manuscript received 18 September 1979, accepted 30 December 1979

The need for a rapid and quantitative separation and estimation of Co^{2+}, Ca^{2+} and PO_4^{3-} ; Cd^{2+}, Ca^{2+} and PO_4^{3-} and Cu^{2+}, Ca^{2+} and PO_4^{3-} was felt during the investigation of these cation exchange reactions in Hydroxyapatite, the prototype of the inorganic constituent of bones and teeth. The present communication has been an attempt to arrive at optimum conditions for such separation and to investigate the suitability of the complexometric titration for their subsequent quantitative determination.

Procedure : To a convenient volume of a weakly acidic (HCl) synthetic solution of Ca^{2+}, Co^{2+}/Cd^{2+} and PO_4^{3-} ions, 5% solution of sodium citrate was added followed by a slight excess of 7%, NH_4CNS solution (for Co^{2+} till the solution was blue), heated just to boiling and to the hot solution 2 ml of pyridine was added. It was shaken well for 5 min and the crystalline precipitates of Co^{2+}/Cd^{2+} was allowed to settle to room temperature, filtered and the precipitate was washed thoroughly with a solution containing 1% pyridine and 1% NH_4CNS. It was then dissolved in minimum volume of 0.6M warm HCl. The solution thus containing Co^{2+}/Cd^{2+} is made up to a known volume, to a convenient aliquot of this solution 0.1 M NaOH was added to just neutral (methyl red indicator for Cd^{2+} and appearence of a slight blue precipitate for Co^{2+}).

In case of Co^{++} the solution after neutralisation was diluted to 100 ml, 5 ml of 5% NaAc was added followed by Murexide indicator. Buffer (NH_4Cl/NH_4OH) $pH\sim10$ was added till the solution was yellow. The Co^{2+} was then determined by titrating against 0.01M E. D. T. A. till a sharp colour change from orange to pure pink was obtained.

In case of Cd^{2+}, to the solution after neutralisation 5 ml of buffer $pH\sim10$ was added followed by 3 drops of Eriochrome Black T indicator and titrated against 0.01 M E.D.T.A. till a sharp colour change from wine red to pure blue resulted. For the Cu^{2+}, Ca^{2+} and PO_4^{3-} system the Cu^{++} in a convenient volume of the solution was precipitated by the addition of a solution containing 32% pyridine and 22% salicylic acid. The precipitate was filtered washed with a solution containing 5% solution of the precipitating reagent. It was dissolved in 0.6M warm HCl. To a known volume of this solution 0.1 M

Table 1—Analyses of Calcium, Copper and Phosphate

Mix No.	Calcium in mg.		Wt% error	Copper in mg.		Wt% error	Phosphorus in mg.		Wt% error
	Expt.	Theo.		Expt.	Theo.		Expt.	Theo.	
I	4.018	4.020	0.049	5.898	5.898	0.00	9.500	9.500	0.00
II	19.640	19.685	0.025	32.087	32.125	0.118	47.500	47.500	0.00
III	10.020	10.025	0.049	15.888	15.899	0.088	23.750	23.780	0.12

Table 2—Analyses of Calcium, Cadmium and Phosphate

Mix No.	Calcium in mg.		Wt% error	Cadmium in mg.		Wt% error	Phosphate in mg.		Wt% error
	Expt.	Theo.		Expt.	Theo.		Expt.	Theo.	
I	40.24	40.22	0.049	11.24	11.232	0.0712	95.94	95.90	0.0417
II	100.20	100.25	0.019	33.72	33.7015	0.0549	47.500	47.500	0.00
III	19.640	19.640	0.00	112.40	112.395	0.0045	9.554	9.554	0.00

Table 3—Analyses of Calcium, Cobalt and Phosphate

Mix. No.	Calcium in mg.		Wt% error	Cobalt in mg.		Wt% error	Phosphate in mg.		Wt% error
	Expt.	Theo.		Expt.	Theo.		Expt.	Theo.	
I	4.018	4.020	0.049	5.893	5.893	0.00	9.500	9.500	0.00
II	100.20	100.22	0.019	17.679	17.678	0.005	47.500	47.500	0.00
III	19.640	19.648	0.041	88.495	88.495	0.001	23.750	23.761	0.046

NaOH was added till neutral followed by 5 ml of buffer $pH \sim 10$. It was diluted to 100 ml and titrated against 0.01 *M* E.D.T.A. using Murexide indicator till a sharp colour change from greenish yellow to deep violet is obtained.

In another set (same for the three systems) from a same amount of the aliquot solution phosphate was precipitated as phosphomolybdate[1], filtered, dissolved in minimum volume of 0.1 *M* hot NaOH. The phosphate was reprecipitated as magnesium ammonium phosphate, separated by filtration, washed with 20% NH_4OH, dissolved in 0.6 *M* warm HCl and subsequently determined complexometrically[2].

In all the cases the filtrate after removal of phosphate as phosphomolybdate was made up to a convenient volume and estimated for the combined cations complexometrically. For the total Ca^{2+} and Cd^{2+}, the procedure adopted was similar for Cd^{2+} as mentioned above except with an additional use of Mg–EDTA complexonate before titration. For the total $Ca^{2+}-Cu^{2+}$ and $Ca^{2+}-Co^{2+}$ ions the free acid was neutralised with 0.2 *M* NaOH and the complexometric procedure adopted was similar with copper and cobalt determinations respectively. The difference of E.D.T.A. consumed for the total cations and the individual titre values resulted in the amount of Ca^{++} present in a given mixture.

The results of chemical analyses of different representative synthetic combination are given in Tables 1-3.

The method is rapid and accurated and can be used for those metal ions which form a solid pyridine-thiocyanate or pyridine-salicylic acid complex.

Acknowledgement

One of the authors (PPM) acknowledges the financial grant by U. G. C.

References

1. N. S. Chickerur and T. S. B. Narasaraju, *Analyst*, 1968, **93**, 844 ; cf. *Z. Anal. Chem.*, 1969, **244**, 324.
2. S. V. Chiranjeevi Rao and N. S. Chickerur, *Z. Anal. Chem.*, 1972, **258**, 367.

Determination of Dissociation Constants of Some Amino Acids. Part I. Use of Wet Volume Ratio Method

LEELA PARDESHI and R. A. BHOBE*

Department of Chemistry, Marathwada University, Maharashtra, India

Manuscript received 11 May 1979, revised 26 November 1979, accepted 4 March 1980

APPLICATION of the ion exchangers of low cross linking as analytical tools is found in the determination of water content of organic solvents and solutions, studies in valencies of various ions

* Senior author to whom all correspondence should be addressed.

in electrolytic solutions, since according to the rise in the valencies the wet volume ratio will shrink proportionately. With the development of new types of ion exchangers[1], containing different active groups such as $-COOH$, $-C{=}N_2$, $-SO_3H$, $-PO(OH)_2$, the possibilities of applying these in analytical procedures have greatly increased. Calvin Calmon[2] has used beads of Permutit QX for determining Ka values of some weak acids. The present authors have adopted the same technique for finding out dissociation constants of some amino acids.

In the present investigation, a 1% DVB cross linking were used (Permutit QX), since it was thought that with 0.5% DVB cross linking a soluble poly-electrolyte may be obtained. Another reason for selecting a higher cross linking of DVB was the greater power of selectivity of such polystyrene beads. Samuelson *et al*[3] have confirmed that the selectivity of the resin phase increases with the degree of cross linking.

Experimental

The amino acids were obtained from British Drug House and were used as such. Permutit QX beads sieved through 30-50 mesh were chosen. The diameters of the beads varied between 0.22 to 0.91 mm. All the measurements of the diameters were made on an Earnest Leitz Wetzlar microscope with a camera Lucida arrangement for drawing. Broken spheres were separated by keeping the Permutit QX beads on a polished inclined plate and tapping the plate gently to roll of the spheres. The split spheres were observed to have stayed behind.

The degree of swelling of the single bead was determined by measuring the diameters in dry and wet state under the microscope. Table 1 below gives the results of swelling with 1 percent cross linking.

TABLE 1—PERCENTAGE OF SWELLING OF BEADS USED, IN H_2O AND C_6H_6

Liquid	Single bead method (% degree of swelling)					
Distilled H_2O	22.79	22.24	22.88	22.86	22.69	22.78
Distilled C_6H_6	3.64	3.70	3.78	3.66	3.88	3.42

The selected beads were first observed under a microscope for their perfect spherical nature. They were washed thoroughly with distilled water and then kept for 24 hours under deionised water. The beads were then labelled and after lightly blotting off the adhered water, their diameters were measured under the microscope. For the purpose of calibration, the labelled beads were then soaked in various concentrations of AnalaR HCl and their dimensions measured before and after soaking. All precautions were taken as recommended in literature[4,5] in measuring microscopically the diameters of the single spheres in dry and wet state. The data are represented graphically in Fig. 1.

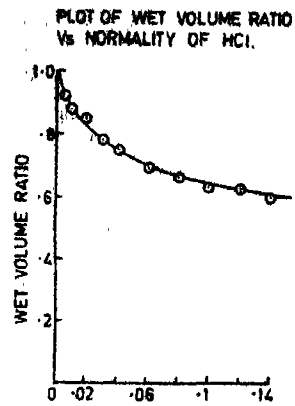


FIG. 1 NORMALITY OF HCl SOLUTION

The wet volume to dry volume ratios for the amino acids studied in this investigation were determined by measuring microscopically the diameters of single spheres in the dry and wet state as done in the case of hydrochloric acid. A wide variation in sizes have been found from sphere to sphere owing, no doubt, to non-uniform polymerisation. Other relevant properties of 1% DVB – cross linking beads are set out in Table 2.

TABLE 2—THE PROPERTIES OF 1% DVB CROSS LINKED PERMUTIT QX EXCHANGER USED

Total exchange capacity	5.19 m. eq. per g.
Density (Dry)	1.17 g/ml (Pyknometer method)
Density (Wet)	47 g/lit (backwash and drain)
Mesh size	30
Degree of swelling	25

Results and Discussion

Fig. 1 is a plot of normality of HCl vs wet volume ratio as drawn from the values obtained. The plot gives the average ratio for three spheres of the given cross linking of a particular concentration of HCl. In the determination of dissociation constants of the quoted amino acids, a single bead was kept in 1 ml 1*N* amino acid with 5 ml of 0.1*N* NaOH added, and then the diameter of the swollen bead was measured under the high power microscope. The bead was washed several times with 1*N* solution of amino acid (with added NaOH) in question, after it attained a maximum diameter as seen under the microscope, the specific solution was blotted out with filter paper and then washed with distilled H_2O. The diameter was rechecked and the process repeated at least six times with the bead to check the reliabilities of the swollen volume. Again,

this was not confined to a single sphere for a specific substance but as often as 4 to 5 spheres were used for determining the size for a particular amino acid. For a particular concentration of amino acid the bead was allowed to come to equlibrium with the solution under investigation by repeated additions of fresh solutions and the removal of the old solution by adsorbing it on fresh filter paper pieces. It was noted that for dilute solution, longer periods of contacts were necessary.

The initial results of Calmon[8] showed that the most deswelling takes place in HCl and the least in acetic acid whose $Ka = 1.75 \times 10^{-5}$ if concentrations of both are identical. Hence it is safe to assume that (1) the volume changes are entirely due to ions, (2) for a given wet volume ratios, concentration of the ions is the same as concentration of very strongly ionised electrolyte at the same volume ratio and, (3) if the volume ratio of an acid under investigation is compared with the volume ratio of HCl of same normality, then the corresponding H^+ ion concentration in the wet volume vs H^+ concentration curve for HCl should give H^+ ions liberated by the unknown acid.

Applying this criterion, H^+ ion concentration of Glycine, L-Proline, DL-Tryptophane, L-Valine, Serine and DL-Methionine were determined (last column, Table 3) and their pKa values were found (Table 3).

TABLE 3—WET VOLUME RATIOS FOR AMINO ACIDS

Amino acid (1 N)	r_1 (um) Wet	r_2 (nm) Dry	Wet-Vol ratio (mean)	H^+ ion con. (from fig. 1)
@ Glycine	0.5815	0.5925		
	0.2525	0.2819	0.720	0.074
	0.6200	0.6902		
@ L-Proline	0.3036	0.3476		
	0.3221	0.3679	0.665	0.101
	0.4075	0.4652		
* DL-Tryptophane	0.4218	0.4777		
	0.5025	0.5702	0.690	0.087
	0.4150	0.4702		
* L-Valine	0.5426	0.6109		
	0.2601	0.2931	0.700	0.0830
	0.4524	0.5101		
@ Serine	0.5928	0.6642		
	0.4026	0.4517	0.710	0.0815
	0.2720	0 2488		
@ DL-Methionine	0.6214	0.6980		
	0.2614	0.2932	0.705	0.0820
	0.8100	0.9101		

@ Soluble in cold water.
* Very soluble in hot water and hence solutions were made accordingly.

It will be observed that average of some three readings in each case has been reported. It is noticed that the H^+ ion concentration of the amino acid bears a linear relation (Fig. 2) with the wet volume ratio of the respective acids and hence it

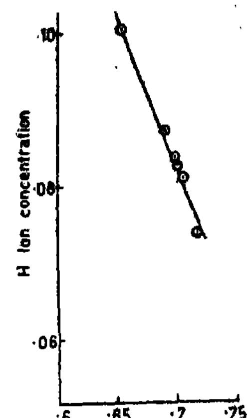


FIG 2 WET VOLUME RATIO OF AMINO ACIDS

should be possible to calculate H^+ concentration of any amino acid in the series without any reference to the HCl wet volume plot.

The dissociation constants were calculated by the standard equation in which concentrations were used in place of activities. The pKa values of amino acids were also determined by potentiometric titrations. The pKa values in addition were obtained by potentiometric methods and are presented in Table 4 along with those obtained by wet volume ratio method. Incidentally, the pKa values obtained by the authors by potentiometry in situ agree well with those reported in literature.

TABLE 4—COMPARISON OF pKa VALUES BY BEAD METHOD AND POTENTIOMETRIC METHOD

Amino acid	pKa (bead method)	pKa (Potentiometric method)
Glycine	9.86	9.98
L-Proline	10.68	10.32
DL-Tryptophane	9.55	9.42
L-Valine	9.72	9.75
Serine	9.24	9.02
DL-Methionine	9.34	9.46

It need not be mentioned here that only second dissociation constants will be obtained in the present case as the amino acids have been rendered into their sodium salts.

Acknowledgement

One of the authors (Leela Pardeshi) is grateful to Dr. K. A. Thakar, Professor and Head, Chemistry Department, Marathwada University for allowing her to carry out post-doctoral work in the Laboratory.

References

1. W. C. BAUMAN and J. EICHBORN, *J. Amer. Chem. Soc.*, 1974, 69, 2830.

2. C. CALMON, *Anal. Chem.* 1953, 25, 491.

3. SAMUELSON *et al.* Ion-Exchange Separation in Analytical Chemistry, John Wiley & Sons, New York, London, 1963, p. 68.

4. H. P. GREGOR, K. M. HELD and J. BELLIN, *Anal. Chem.*, 1951, 23, 620.

5. L. SAUNDERS and R. S. SHRIVASTAV, *J. Chem. Soc.*, 1952, 2111.

6. E. J. COHN and J. T. EDSALL, "Protein, Amino acid and Peptiles" Reinhold Publishing Corp., New York, 1948.

Sorption and Desorption Studies of Crystal Violet and Malachite Green on and from Synthetic Zeolites 3A and AW500

SATI PRASAD BANERJEE

Department of Chemistry, University of Saugar, Sagar-470 003, M.P.

Manuscript received 27 November 1979, accepted 20 December 1979

CRYSTAL violet and malachite green, which are triphenylmethane dyes, were used for interaction with synthetic zeolites 3A and AW500. The interacted samples have been studied by thermogravimetric, photometric and infrared spectroscopic methods. The zeolite 3A was in powder form while the other was in 1/16″ cylindrical pellet form. Their characteristics are known from earlier studies[1-3].

Experimental

The zeolites were kept in contact with aqueous solutions of the two dyes for several days. They were heated from time to time to effect maximum interaction and later kept inside the refrigerator also for several days. The zeolites were filtered off from the excess liquid and dried in air. The thermogravimetric studies were carried out on a thermobalance supplied by the Fertilizer Corporation of India, Sindri, at a heating rate of 10°/minute between 293 and 1073°K. Absorption data were collected between 200 and 1000 nm by means of a spectrophotometer with reflectance attachment (Model VSK-2P). The IR spectra were recorded on a Perkin-Elmer instrument (Model 577) between 4000 and 200 cm^{-1} in cesium iodide. The elemental analyses were done on a Thomas CH-Analyzer 35 and Coleman N-Analyzer 29. The relevant data have been reproduced in Table 1.

Discussion

The zeolite samples start losing weight around 353°K and process of weight loss continues till 873°K for malachite green-sorbed AW500 and 933°K for the other three samples. Maximum weight loss for dehydration occurs around 430°K and for the desorption of the dyes at about 530°K. Thermogravimetric data were utilised for evaluating the kinetic parameters of the weight loss sequence, on the basis of the relation, $g(\alpha)=[-\log_e(1-\alpha)]^{1/n}=Kt=ze^{-E/RT}$, suggested by Avrami[4] and Erofeyev[5] where K is the specific reaction rate constant and E is the corresponding activation energy of the isothermal process. Values of α were calculated from

$$\alpha=\frac{(W_t-W_f)}{(W_o-W_f)}$$

where W_t is the indicated weight at time or temperature, t ; W_o is the initial sample weight ; and W_f is the residual weight at the end of the process under study. The plots between $g(\alpha)$ and time are nonlinear for n=1, 2 and 3. These plots show that the thermal events occur at two different rates. The plots for $\log_e [g(\alpha)/T^2]$ vs 1000/T are straight lines having different slopes for dehydration and desorption of sorbed species for n=1, 2 and 3. Both the processes are first order reactions[6]. The extent of dye-sorption is obtained from the photometric data as well as the percentages of carbon in the various samples. It is clear that crystal violet is more extensively sorbed than malachite green and zeolite 3A exhibits greater capacity for dye-sorption compared to AW500. IR spectra of the samples indicate that the sorption occurs by hydrogen bonding atleast in the case of 3A as the absorption bands due to water at about 3500 and 1650 cm^{-1} are broadened considerably due to the presence of the sorbed species. This broadening effect is not pronounced in the case of zeolite AW500.

TABLE 1

Zeolite	Weight Loss %	Carbon %	Hydrogen %	Nitrogen %
Crystal violet sorbed 3A	28.5	4.88	2.76	Negligible
Crystal violet sorbed AW500	18.7	1.70	2.24	,,
Malachite green sorbed 3A	23.9	1.34	1.84	,,
Malachite green sorbed AW500	16.6	Negligible	1.57	,,

Acknowledgement

The author is grateful to the Union Carbide Corporation, U.S.A., for the gift of the zeolite samples and to the U.G.C., New Delhi, for a research grant.

References

1. T. B. REED and D. W. BRECK, *J. Amer. Chem. Soc.*, 1956, **78**, 5972.
2. MALTI SRIVASTAVA and SATI PRASAD BANERJEE, *J. Inst. Chemists (India)*, 1978, **50**, 264.
3. RAVEENDRAN K. KANIPPAYOOR and SATI PRASAD BANERJEE, *Cent. Glass Ceram. Res. Inst. Bull.*, 1979, **26**, in press.
4. M. AVRAMI, *J. Chem. Phys.*, 1941, **9**, 177.
5. B. V. EROFEYEV, *Compt. Rend.*, 1946, **52**, 511.
6. A. W. COATS and J. P. REDFERN, *Nature*, 1964, **201**, 68.

Effect of Non-Aqueous Solvents on Depolarising Action of Cadmium (II)-N-[(β-Aminoethyl)]-Ethanolamine Complexes at D.M.E.*

SHIVENDRA PATHAK

P. G. Deptt. of Chemistry, S.G.N. Khalsa College, Sri Ganga nagar

Manuscript received 19 February 1979, revised 29 January 1980, accepted 4 March 1980

THE electrochemical studies of cadmium(II)-N-[(β-aminoethyl)]-ethanolamine complexes have been carried out at dropping mercury electrode. Two complexes with metal to ligand ratio as 1 : 1 and 1 : 2 have been reported at *p*H 6.6 ± 0.1 and temperature 303°K. Stepwise formation constants of cadmium(II)-N-[(β-aminoethyl)]-ethanolamine complexes have been determined in both aqueous and aqueous non-aqueous mixed media. The studies have also been extended to the effect of formamide, dimethylsulphoxide (DMSO), methanol, *n*-propanol and isopropanol on the formation constants of the complexes. The effects of ligand concentration on complexation reaction have been examined in terms of relative distribution of metal and ligand in solution.

The importance of amines and several other nitrogen-containing compounds has been recognised in the biochemical, analytical and pharmaceutical fields. Electroanalytical investigation of various metal ions with nitrogen-containing ligands are thus useful and recently studied by a number of workers[1-4]. However, there is no reference to the pursuit of polarographic studies on the cadmium-(II)-N-[(β-aminoethyl)]-ethanolamine complexes, therefore, the present investigation were undertaken.

* Presented in 49th Annual Session of National Academy of Sciences.

Experimental

A manual polarograph with a scalamp galvanometer acting as a current recorder was used in all the investigations. The dropping mercury electrodes had the characteristics $m = 1.8$ mg. sec^{-1} and $t = 4.3$ sec. (open circuit). Chemicals used were of reagent grade. The solvents were purified, wherever necessary, by standard methods.

In each system the concentration of Cd(II) was $5 \times 10^{-4} M$. Ionic strength (μ) was 1.0*M* maintained constant by adding requisite amounts of sodium perchlorate in all the test solutions. The *p*H was maintained 6.6±0.1 by Toshiniwal *p*H meter. Purified nitrogen was presaturated with the given aqueous-nonaqueous solvent mixture was passed for thirty minutes to remove dissolve oxygen in each test solution. Temperature was kept constant at 303°K by the help of Haake type ultrathermostat.

Results and Discussion

The reversibility of reduction with involvement of two electrons and with controlled diffusion in aqueous and aquo-nonaqueous mixed media were concluded for cadmium-N-[(β-aminoethyl)] ethanolamine system, from the slopes (31±1) of log plots and proportionality of i_d and $\sqrt{h}$ respectively at 303°K.

To investigate the effect of change of ligand concentration, polarograms of ·05 m*M* cadmium(II) mixed with various concentration (0.0 to 0.05*M*) of N-[(β-aminoethyl)]-ethanolamine were recorded. The shift in half-wave potential to more negative values, alongwith a decrease in diffusion current (i_d) on increasing ligand concentration, indicated the formation of complexes in each system. The nature of wave did not change at higher concentrations of ligand.

The values of overall formation constants, evaluated by DeFord-Hume's method[6] are comprehended below :

Overall formation Constants of Cd(II)-N-[(β-aminoethyl)]-ethanolamine Complexes by DeFord-Hume's Method.

Solvent Media	log β_1	log β_2
Pure aqueous	7.14	9.36
40% Methanol + Aqueous	8.54	9.07
60% Methanol + Aqueous	9.11	9.54
25% DMSO + Aqueous	8.74	10.00
40% DMSO + Aqueous	9.47	11.18
40% Isopropanol + Aqueous	6.84	7.80
60% Isopropanol + Aqueous	6.92	8.14
25% N-Propanol + Aqueous	7.00	7.81
40% N-Propanol + Aqueous	6.89	7.63
25% Formamide + Aqueous	6.25	7.69
40% Formamide + Aqueous	6.90	7.20
60% Formamide + Aqueous	6.84	7.11

It has been observed from the values of overall formation constants that the increase in percentage of methanol and DMSO makes the values of overall formation constant to increase. This may be attributed to the less solvation of the cadmium ion by methanol or DMSO than by water, if solvation is considered to be the only factor affecting the overall formation constant[8,9]. Otherwise there are many other factors which can affect formation constant viz. density, dielectric constant[9], viscosity[10], may also be effective in this regard. Moreover ion-pair formation[11] plays its role in this case. The increase in the values of overall formation constants in aqueous-nonaqueous media is in complete agreement with similar studies by other workers[12,13].

In case of isopropanol-water, *n*-propanol-water and formamide water mixed media of various compositions, the values of overall-formation constants are less than those are in pure water.

The relative distribution of the simple Cd(II) and complexed with N-[(β-aminoethyl)]-ethanolamine as function of ligand concentration advocates that the amount of Cd(II) decreases as ligand concentration increases[7].

References

1. D. N. Chaturvedi and C. M. Gupta, *Z. Analyt. Chem.*, 1972, **260**, 120.
2. P. C. Rawat and C. M. Gupta, *Indian J. Chem.*, 1973, **11**, 186.
3. P. K. Migal and K. Hayashi, *J. Electroanal. Chem.*, 1965, **10**, 2513.
4. P. K. Migal, *Russ. J. Chem.*, 1962, **7**, 675.
5. Dayanand Chaturvedi and C. M. Gupta, *Analyst*, 1973, **98**, 895.
6. D. D. DeFord and D. N. Hume, *J. Amer. Chem. Soc.*, 1951, **73**, 5321.
7. Shivendra Pathak, Ph. D. Thesis, University of Rajasthan, Jaipur (India), 1977.
8. D. L. Mc. Masters, R. B. Dunlap, L. W. Kreider and T. R. Shearer, *Anal. Chem.*, 1967, **39**, 103.
9. J. L. Jones and H. A. Fritsche, *J. Electroanal. Chem*, 1966, **13**, 384.
10. M. Muller, "The Polarographic Methods of Analysis, Chemical Education Publishing, Easton, Philadelphia, 1951, p. 74.
11. W. B. Schaap, *J. Amer. Chem. Soc.*, 1960, **82**, 1837.
12. S. E. Manahari and R. T. Iwamota, *J. Electroanal. Chem.*, 1967, **14**, 213.
13. K. Kodama and K. Hayashi, *J. Electroanal. Chem.*, 1967, **14**, 209.

Synthesis of *p*-Alkyl-(2-benzimidazolyl)-methyl-aminobenzoates and Corresponding Hydrazides as Possible Antimalarial Agents

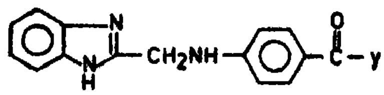
SURENDRA BAHADUR and K. K. PANDEY

Chemistry Department, Lucknow University, Lucknow-226 007

Manuscript received 9 February 1979, revised 24 September 1979, accepted 9 January 1980

A series of esters of *p*-(2-Benzimidazolyl)methylaminobenzoic acid (I, Y=OR) has been synthesised. One such ester (Y=OEt) on hydrazinolysis furnished the corresponding hydrazide (I, Y=NH.NH_2) which when condensed with different aromatic aldehydes yielded Schiff's bases (I, Y=NH.N.=CHR). Reduction of Schiff's base with sodium-borohydride proceeded smoothly to give I (Y=NH.$NHCH_2R$). Representative compounds when screened, were found inactive as antimalarial.

A number of benzimidazoles have been synthesised and tested as antimalarial agents[1,2]. It was, therefore, considered worthwhile to synthesise such substituted benzimidazole derivatives containing *p*-aminobenzoic acid. The different esters and hydrazides of *p*-(2-benzimidazolyl)methylaminobenzoic acid have been prepared[3]. The hydrazide was then condensed with aldehydes[4] and the Schiff's bases thus obtained were reduced to the corresponding secondary amines[5].



I

Bio-Assay :

Eleven compounds were screened for antimalarial activity against *P.berghei*-Albino Mice (Swiss) model. None of them was found to be active as antimalarial.

Specification of Host-(Wt=18-20 gm), sex-male Inoculum : 1×10 infected Red cells/animal in 0.25 ml.

Experimental

Melting points were determined in open capillaries and are not corrected. Infrared were recorded on a Perkin-Elmer 137G spectrophotometer in KBr.

Ethyl-p-(2-benzimidazolyl)methylaminobenzoates ; (I, Y=OC_2H_5)

Equimolar quantities of 2-chloromethyl-benzimidazole and ethyl-*p*-aminobenzoate were refluxed in ethanol in presence of small amount of sodium iodide for 12 hr. The solid separated on cooling

TABLE 1—PHYSICAL DATA OF I

Compound No.	Y	Molecular formula	M. Pt. °C	Yield %
1.	$-OCH_3$	$C_{16}H_{15}N_3O_2$	283	50
2.	$-OEt$	$C_{17}H_{17}N_3O_2$	265	50
3.	$-OPr$	$C_{18}H_{19}N_3O_2$	222	60
4.	$-OBu$	$C_{19}H_{21}N_3O_2$	216	50
5.	$-NHNH_2$	$C_{15}H_{15}N_5O$	240	70
6.	$NHN=CH.C_6H_4OH$-(*o*)	$C_{22}H_{19}N_5O_2$	244	50
7.	$NHN=CH.C_6H_4.NO_2$(*m*)	$C_{22}H_{18}N_6O_3$	248	40
8.	$NHN=CH.C_6H_4.Br$(*p*)	$C_{22}H_{18}N_5OBr$	230	45
9.	$NH.N=CH.C_6H_5$	$C_{22}H_{19}N_5O$	246	60
10.	$NH.N=CH.C_6H_3.OCH_3$(*m*)-OH(*p*)	$C_{23}H_{21}N_5O_3$	252	60
11.	$NH.N=CH.C_6H_4.NO_2$(*p*)	$C_{22}H_{18}N_6O_3$	225	50
12.	$NH.N=CH.C_6H_4.Cl$(*p*)	$C_{22}H_{18}N_5Cl$	238	55
13.	$NH.N=CH.C_6H_4.NO_2$(*o*)	$C_{22}H_{18}N_6O_3$	228	50
14·	$NH.N=CH.C_4H_3O$(*o*)	$C_{20}H_{17}N_5O_2$	232	60
15.	$NH.N=CH.C_6H_4.OH$(*p*)	$C_{22}H_{19}N_5O_2$	255	80
16.	$NH.NH.CH_2.C_6H_4OH$(*o*)	$C_{22}H_{21}N_5O_2$	240	80
17.	$NH.NH.CH_2.C_6H_4NO_2$(*m*)	$C_{22}H_{20}N_6O_3$	242	80
18.	$NH.NH.CH_2.C_6H_4Br$(*p*)	$C_{22}H_{20}N_5OBr$	238	80
19.	$NH.NH.CH_2.C_6H_5$	$C_{22}H_{21}N_5O$	242	80
20.	$NH.NH.CH_2.C_6H_3.OCH_3$(*m*)OH(*p*)	$C_{23}H_{23}N_5O_3$	235	80
21.	$NH.NH.CH_2.C_6H_4.NO_2$(*p*)	$C_{22}H_{20}N_6O_3$	232	80
22.	$NH.NH.CH_2.C_6H_4.Cl$(*p*)	$C_{22}H_{20}N_5OCl$	233	80
23.	$NH.NH.CH_2C_6H_4\ NO_2$(*o*)	$C_{22}H_{20}N_6O_3$	234	80
24.	$NH.NH.CH_2C_4H_3O$(*o*)	$C_{20}H_{21}N_5O_2$	242	80
25.	$NH.NH.CH_2.C_6H_4OH$(*p*)	$C_{22}H_{21}N_5O_2$	248	80

a. The elemental analyses were within satisfactory limits.
b. IR: 1. 2.90(NH), 5.8(C=O), 6.2(C=N), 6.8-7 (alkyl)
5. 3.0(NH), 5.95(C=O), 6.25(C=N)
13. 3.10(NH), 6.0(C=O), 6.2(C=N), 6.60 and 7.60(NO_2).
c. All the compounds were recrystallised from ethanol.

was filtered and washed with ethanol and recrystallised. Me, Pr, Bu esters were also prepared in the same way.

p-(2-Benzimidazolyl)methylaminobenzoic acid hydrazide (I, Y=NH.NH₂)

Ethyl-*p*-(2-benzimidazolyl)methylaminobenzoate (0.01 mole) and hydrazine hydrate (0.02 mole) were refluxed in absolute ethanol for 10 hr. Excess of solvent was removed and the hydrazide, thus separated, was filtered and recrystallised from ethanol.

Hydrazones (I, Y=NH.N=CHAr)

Equimolar quantities of hydrazide and aldehyde were refluxed in ethanol, containing 3 drops of AcOH, for 6 hr. The solid separated was filtered and recrystallised.

Reduction of hydrazones : formation of I(Y=NH.NH.CH₂Ar)

A 10% methanolic solution of sodium borohydride was added with stirring into a 10% methanolic solution of Schiff's base during 30 min. The mixture was heated for 15 min under reflux. Excess of methanol was removed and the secondary amine was isolated by the addition of water. It was filtered and recrystallised.

Acknowledgement

The authors wish to acknowledge their thanks to the Head, Chemistry Department, Lucknow University, Lucknow for providing necessary facilities, to C.D.R.I. for Microanalyses and IR and to Dr. G. P. Dutta, C. D. R. I. Division of Microbiology, C. D. R. I. for screening of compounds. K. K. P. is grateful to C. S. I. R., New Delhi for financial assistance.

References

1. F. R. BUSFORD, F. H. S. CURD, F. L. ROSE and Imperial Chemical Industries Ltd., British Patent 598, 499; *Chem. Abs.* 1948, **42**, 2291.
2. S. J. YAN, W. H. BURTON, *et al. J. Het. Chem.*, 1978, **15**(2), 297-300.
3. F. E. KING, R. M. ACHESON and P. C. SPENSLEY, *J. Chem Soc.*, 1949, 1403.
4. D. W. BOYKIN and R. S. VARMA, *J. Med. Chem.*, 1970, **13**, 583.
5. JOHN H. BILLMAN and ARTHUR C. DIESINO, *J. Org. Chem.*, 1957, **22**, 1068.
6. W. H. O. Technical Report Series 1973, no. 529. Chemotherapy of malaria and resistance to antimalarials.

Search for New Anthelmintics—Part I. Synthesis on Some N^1-(Arylaminothiocarbonylthioacetyl)-N^3-aryl Ureas

A. K. RAMRAKHYANI and PRADEEP KUMAR

Department of Chemistry, Feroze Gandhi (P. G.) College, Rae Bareli-229 001

Manuscript received 19 October 1978, revised 6 August 1979, accepted 4 March 1980

THIRTY new N^1-(arylaminothiocarbonylthioacetyl)-N^3-aryl ureas have been synthesized by condensing the ammonium salt of various dithiocarbamic acids with chloroacetyl ureas in aqueous acetone. Nine of these compounds have been screened against *H. nana* and *N. brasiliensis* infections in rats.

Esters of dithiocarbamic acids have clearly been established as the leading anthelmintics[1-2]. A large number of urea derivatives have appeared in recent literature as potent anthelminitics[3-5]. Hence the synthesis of title ureas was undertaken.

Experimental

All the melting points are uncorrected. Substituted phenyl ureas were prepared by treating an appropriate amine with a solution of potassium cyanate according to the method of Berlinerblau[6]. 1-Chloroacetyl-3-arylureas were prepared by the method of Jacob *et al*[7]. Ammonium salts of various dithiocarbamic acids were prepared by following a published procedure[8].

N^1-(Arylaminothiocarbonylthioacetyl)-N^3-aryl ureas :

1-Chloroacetyl-3-aryl urea (0.01 mole) and an appropriate ammonium dithiocarbamate (0.01 mole) were dissolved in 100 ml of aqueous acetone and the mixture was refluxed on a water bath for 3 hrs. The acetone was then distilled off, and the crude solid obtained was washed with cold water and recrystallised from acetone (Table 1). All the compounds showed consistent nitrogen analyses.

TABLE 1

$$RC_6H_4NHC(=S)-SCH_2CONHCONHC_6H_4R^1$$

Sl. No.	R	R′	M.P. °C	Yield %
1.	H	4-OCH_3	141	72
2.	H	4-Cl	140	75
3.	2-CH_3	3-CH_3	139	73
4.	2-CH_3	4-OCH_3	134	74
5.	2-CH_3	2-Cl	133	68
6.	2-CH_3	4-Cl	135	74
7.	3-CH_3	2-CH_3	105	80
8.	3-CH_3	3-CH_3	110	71
9.	3-CH_3	4-CH_3	160	72
10.	3-CH_3	2-OCH_3	132	70
11.	3-CH_3	2-Cl	143	72
12.	3-CH_3	4-Cl	140	70
13.	4-CH_3	3-CH_3	129	72
14.	4-CH_3	4-Cl	132	80
15.	2-OCH_3	3-CH_3	135	69
16.	2-OCH_3	4-CH_3	127	80
17.	2-OCH_3	2-Cl	130	72
18.	2-OCH_3	4-Cl	133	72
19.	4-OCH_3	2-CH_3	140	71
20.	4-OCH_3	4-CH_3	135	68
21.	4-OCH_3	2-OCH_3	132	68
22.	4-OCH_3	2-Cl	134	70
23.	4-OCH_3	4-Cl	135	72
24.	3-Cl	H	144	73
25.	3-Cl	4-CH_3	133	79
26.	3-Cl	2-OCH_3	134	71
27.	3-Cl	4-Cl	143	70
28.	4-Cl	H	130	74
29.	4-Cl	4-CH_3	145	70
30.	4-Cl	4-Cl	135	68

Bio-assay :

Nine compounds numbered 1, 3, 4, 8, 9, 10, 15, 20, 21 (Table 1) have been screened against *H. nana* and *N. brasiliensis* infection in rats, according to the method of Whitlock[10]. These compounds were administered orally at a dose of 250 mg/Kg × 1 in case of *H. nana* and 250 mg/Kg × 3 in case of *N. brasiliensis*. None of them, however, showed any significant activity.

Acknowledgement

Grateful acknowledgement of the authors is due to the I. C. M. R., New Delhi for providing Junior Research Fellowship to P. K. They are also thankful to Dr. J. C. Katiyar, Division of Parasitology, C. D. R. I., Lucknow for his keen interest in the present work.

References

1. R. C. TWEIT, R. D. MUIR, S. MIZUBA and W. R. CROWLEY, *J. Med. Chem.*, 1969, **12**, 343.
2. FARBWERKE HOECHST. A. G., *Fr. Demande*, 2, 015, 026, 1970 ; *Chem. Abs.*, 1971, **75**, 5534.
3. J. R. GEIGY, *Neth. Appl.*, 1965, **6**, 407, 900 ; *Chem. Abs.*, 1965, **63**, 440.
4. J. S. RUHOFF, *U. S.*, 2, 983, 646, 1961 ; *Chem. Abs.*, 1961, **61**, 18022.
5. A. DAVID EICHLER, M. S. JOSHUA LUCAS, C. J. GEORGE MARTIN, W. EDGAR PARNELL, Garth Molesdale Thompson and F. RONALD PHILLIPSON, *Ger. Offen.* 2, 129, 960, 1971 ; *Chem. Abs.*, 1972, **76**, 72281.
6. BERLINERBLAU, *J. Pract. Chem.*, 1889, (2), **30**, 103.
7. W. A. JACOB, M. HEIDELBERGER and I. P. ROLF., *J. Amer. Chem. Soc.*, 1919, **41**, 458.
8. A. I. VOGEL, A Text Book of Practical Organic Chemistry, Longmans Group Ltd., 1957, 643.
9. J. S. STEWARD, *Parasitology*, 1955, **45**, 255.
10. J. S. WHITLOCK, *Parasitology*, 1948, **29**, 42.

Carbon-13 NMR Spectra of Some Chromeno-Imidazole Derivatives

C. K. GHOSH

Department of Biochemistry, University College of Science, Calcutta-700 009

and

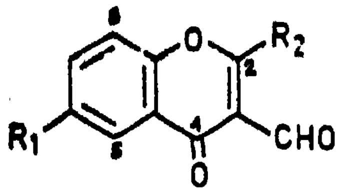
A. K. MITRA and A. PATRA

Department of Chemistry, University College of Science, Calcutta-700 009

Manuscript received 24 July 1979, accepted 4 March 1980

IN an earlier communication[1] the reactions of chromon-3-carboxylaldehyde (I) and 6-methyl chromon-3-carboxylaldehyde (II) with benzil and NH_4Ac in glacial HOAc were reported. The former afforded a product which was assigned 3(4',5'-diphenylimidazole-2'-yl)-4(H)-oxo-1-benzopyran structure (III) in preference to 1H-2,3-diphenyl-5-hydroxy-6-(2'-hydroxy benzoyl)-1,4-diazepine (IV) or its tautomer V mainly on the basis of ¹H-NMR spectral data. The product from II was similarly assigned the structure VI. We report here the more convincing Carbon-13 NMR* data for the aforesaid reaction products of I and II as well as those of VII and VIII, supporting the formations of imidazoles III, VI, IX and X respectively. J_{C-H} for I, III, VI, IX and X are also reported. IX and X were obtained from VII and VIII respectively in a manner reported previously[1] for the preparations of III and VI.

A comparison of the Carbon-13 NMR signals and J_{C-H} (Table 1) for the different carbons of III with those of I strongly suggested the presence of 3-substituted chromone moiety in III. In addition to the signals for the carbons of the phenyl rings, the spectrum of III also displayed two weak singlets in the region 130-140 ppm in agreement with the presence of a fully substituted imidazole ring. Compounds VI, IX and X exhibited signals accountable for the appropriate substitution at C-6.



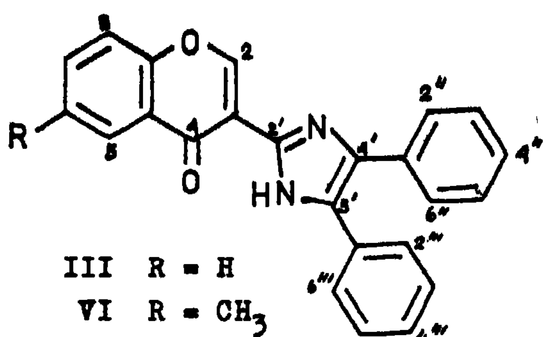
I $R_1 = R_2 = H$

II $R_1 = CH_3$, $R_2 = H$

VII $R_1 = Cl$, $R_2 = H$

VIII $R_1 = Br$, $R_2 = H$

XI $R_1 = H$, $R_2 = NH_2$

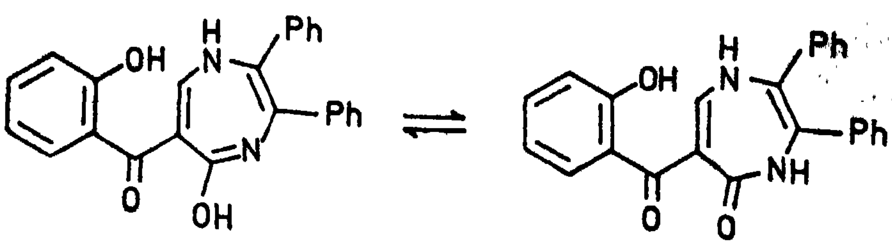


III R = H

VI $R = CH_3$

IX R = Cl

X R = Br



IV ⇌ V

---

* Carbon-13 NMR spectra were run in $CDCl_3$ ($\delta_{TMS} = \delta_{CDCl_3} + 76.9$ ppm) on a Varian CFT-20 NMR spectrometer operating at 20.1 MHz in the FT mode and chemical shifts are in δ(ppm). In each case a proton noise decoupled and single frequency off-resonance decoupled spectra were run to establish the carbon shifts and the degree of protonation. Coupled spectra afforded the J_{C-H} values (Hz).

The C-4 carbonyls in all the compounds appeared in the region of 175 ppm. The chemical shifts of C-2 and C-3 carbons of the compounds III, VI, IX and X occurred in the region of 155 and 114 ppm respectively, whereas downfield shifts were observed for C-2 and C-3 in I and XI due to the presence of −CHO group at C-3. C-8 carbons in all the compounds resonated at the same regions irrespective of the *meta* substituents in the phenyl ring. C-4a carbons in the compounds III, VI, IX and X appeared in the rigion of 124 ppm whereas it absorbed at about 120 ppm for the compounds I and XI. C-5 and C-7 resonated uniformly in all the compounds except for the compounds VI and X where downfield shifts of about 1.5 ppm and about 3 ppm respectively were observed due to *ortho* effect[2]. The chemical shifts of C-6 in all the compounds were in conformity with their structures: compounds I, III and XI absorbed in the same region but downfield shift of ~10 ppm and ~6 ppm and an upfield shift of ~5.5 ppm were observed for the compounds VI, IX and X respectively for the substituent effects of CH_3, Cl and Br groups at C-6. Chemical shifts of C-8a in all the compounds appeard nearly at the same position. The chemical shifts for C-2', C-4' and C-5' and those of phenyl ring carbons were uniform and in conformity with their structures.

The one bond coupling constants (J_{C-H}) of the oxygenated carbon C-2 in III, VI, IX and X was about 200 Hz which was closely comparable to the J_{C-H} for C-2 in I, indicating that C-2 was not fully substituted. J_{C-H} for aromatic and methyl carbons were in the normal range.

TABLE 1—CARBON-13 CHEMICAL SHIFTS AND COUPLING CONSTANTS (J_{C-H}) OF I, III, VI, IX, X AND XI

	I	III	VI	IX	X	XI*
C-2	160.4	154.6	155.0	154.6	154.6	165.6
	(198.1)	(200.1)	(199.6)	(201.0)	(201.1)	
C-3	125.0	113.7	113.0	114.1	114.2	122.3
C-4	175.6	175.8	175.8	174.8	174.6	175.3
C-4a	120.1	123.5	123.1	124.5	124.8	120.0
C-5	126 3	125.5	124.8	125.0	128.4	125.4
	(164.0)	(166.5)	(164.0)	(161.6)	(161.1)	
C-6	125.8	125.4	135.7	131.6	119.1	125.3
	(160.5)	(166.7)				
C-7	134.6	133.7	135.2	134.0	136.8	134.2
	(164.0)	(164.2)	(164.0)	(169.0)	(168.2)	
C-8	118.4	118.1	117.9	119.9	120.1	116.9
	(167.4)	(166.1)	(165.1)	(168.1)	(168.8)	
C-8a	155.9	155.7	154.0	154.0	154.5	
C-2'		139.5	139.7	139.1	139.1	
C-4', 5'		132.6	131.4	131.6	132.0	
C-1'', 1'''		127.5	127.5	127.5	127.5	
C-2'', 2''', 6'', 6'''		127.5	127.5	127.5	127.5	
		(162.2)	(162.0)	(159.8)	(159.7)	
C-3'', 3''', 5'', 5'''		128.3	128.3	128.4	128.4	
		(160.2)	(160.4)	(160.5)	(161.1)	
C-4'', 4'''		127.1	127.8	127.2	127.2	
		(160.7)	(159.4)	(160 5)	(160.7)	
CHO	188.2					188.1
	(186.5)					
CH_3			20.7			
			(125.2)			

* In d_6-DMSO; C-8a signal merged with noise.

References

1. G. K. Ghosh and D. K. Sinha Roy, *Indian J. Chem.*, 1978, 16B, 797.
2. J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, 1972.

Search for Potent Anthelmintics-Part XIV. Benzoxazolylthio/Oxyethylureas and Thioureas

Md. IMTIAZ HUSAIN* and SADA NAND MISRA

Department of Chemistry, Lucknow University, Lucknow-226 007

Manuscript received 4 April 1979, revised 24 September 1979, accepted 9 January 1980

A number of N^1-(2-benzoxazolylthio/oxyethyl)-N^3-alkyl/arylureas and thioureas were synthesised as possible anthelmintics.

Several thioureas[1,2] including benzimidazolyl thioureas[3] have very recently been found as effective anthelmintics. A few ureas[4,5] have also been known to reduce hook worms in dogs and possess nematocidal effect against Panegrellus redivivus. Moreover, some benzoxazole derivatives[6,7] exhibited anthelmintic properties in mice and chickens. In view of these findings, it was considered desirable to synthesise the title ureas and thioureas with a view to determining their anthelmintic efficacy.

Benzoxazol-2-thione/one[8,9] was refluxed with β-chloroethanolamine hydrochloride[10] in the presence of acetone and anhydrous K_2CO_3 to afford 2-(2-aminoethylthio/oxy) benzoxazole. The latter was treated with various alkyl/aryl isocyanates or isothiocyanates to furnish the desired ureas and thioureas.

The results of anthelmintic screening of these compounds will be communicated later on.

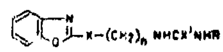
Experimental

All melting points are uncorrected. I.R. spectra were recorded on Perkin-Elmer spectrophotometer in KBr pellets.

I. 2-(2-Aminoethylthio)benzoxazole and 2-(2-aminoethoxy) benzoxazole:

A mixture of benzoxazol-2-thione or benzoxazol-2-one (.01 mole), β-chloroethanolamine hydrochloride (.01 mole), anhydrous K_2CO_3 (.02 mole) and acetone (100 ml) was refluxed for 16 to 20 hr on a steam bath. It was then cooled and filtered. Acetone was distilled off from the filtrate and the crude product obtained was recrystallised from benzene-petroleum ether.

TABLE 1



Sl. No.	X	X[1]	n	R	M.P. °C	Yield %	Molecular formula	%Nitrogen Found	%Nitrogen Calcd.
1.[a]	S	O	2	C_6H_5	232	60	$C_{16}H_{15}N_3O_2S$	13.04	13.42
2.[b]	S	O	2	CH_3	145	65	$C_{11}H_{13}N_3O_2S$	16.16	16.73
3.	S	S	2	C_6H_5	135	52	$C_{16}H_{15}N_3OS_2$	12.92	12.76
4.[c]	S	S	2	p-ClC_6H_4	120	48	$C_{16}H_{14}ClN_3OS_2$	11.11	11.55
5.	S	S	2	p-BrC_6H_4	85	50	$C_{16}H_{14}BrN_3OS_2$	10.72	10.29
6.	S	S	2	o-$CH_3C_6H_4$	170	62	$C_{17}H_{17}N_3OS_2$	12.54	12.24
7.	S	S	2	m-$CH_3C_6H_4$	128	50	$C_{17}H_{17}N_3OS_2$	11.81	12.24
8.	S	S	2	p-$CH_3C_6H_4$	145	68	$C_{17}H_{17}N_3OS_2$	12.52	12.24
9.	S	S	2	o $CH_3OC_6H_4$	154	55	$C_{17}H_{17}N_3O_2S_2$	11.98	11.69
10.	S	S	2	p-$CH_3OC_6H_4$	122	66	$C_{17}H_{17}N_3O_2S_2$	11.27	11.69
11.	S	S	2	α-$C_{10}H_7$	125	60	$C_{20}H_{17}N_3OS_2$	11.46	11.08
12.	S	S	2	C_6H_{11}	130	65	$C_{16}H_{21}N_3OS_2$	12.16	12.54
13.	O	O	2	C_6H_5	80	55	$C_{16}H_{15}N_3O_3$	14.50	14.14
14.	O	S	2	C_6H_5	68	50	$C_{16}H_{15}N_3O_2S$	13.10	13.42
15.[d]	O	S	2	p-BrC_6H_4	78	58	$C_{16}H_{14}BrN_3O_2S$	11.20	10.71
16.	O	S	2	o-$CH_3C_6H_4$	135	60	$C_{17}H_{17}N_3O_2S$	12.52	12.84
17.[e]	O	S	2	m-$CH_3C_6H_4$	110	65	$C_{17}H_{17}N_3O_2S$	12.43	12.84
18.	O	S	2	p-$CH_3C_6H_4$	86	62	$C_{17}H_{17}N_3O_2S$	13.29	12.84
19.	O	S	2	o-$CH_3OC_6H_4$	84	54	$C_{17}H_{17}N_3O_2S$	12.70	12.24
20.	O	S	2	p-$CH_3OC_6H_4$	92	56	$C_{17}H_{17}N_3O_2S$	12.61	12.24
21.[f]	O	S	2	α-$C_{10}H_7$	90	62	$C_{20}H_{17}N_3O_2S$	11.98	11.57
22.	O	S	2	C_6H_{11}	106	66	$C_{16}H_{21}N_3O_2S$	13.54	13.17

I.R. Spectral Bands in cm^{-1}

	amide C=O	$-SCH_2-$	NH-Str.	$-\underset{\|\atop S}{C}-N$	$-O-CH_2-$
a	1650	1430	3300	—	—
b	1650	1415	3300	—	—
c	—	1418	3170	1090	—
d	—	—	3160	1150	1290
e	—	—	3100	1145	1260
f	—	—	3100	1050	1250

Analysis and m.p.'s of the above two compounds thus prepared are given as follows :

i. 2-(2-Aminoethylthio)benzoxazole, m.p. 160° (Found : N, 14.12 ; $C_9H_{10}N_2OS$ requires N, 14.43%)

ii. 2-(2-Aminoethoxy)benzoxazole, m.p. 120° (Found : N, 15.36 ; $C_9H_{10}N_2O_2$ requires N, 15.73%)

II. *N[1]-(2-benzoxazolylthio/oxyethyl)-N[3]-alkyl/arylureas and thioureas :*

2-(2-Aminoethylthio/oxy)benzoxazole (0.01 mole) and alkyl/aryl isothiocyanate or isocyanate (0.01 mole) were refluxed in anhydrous benzene (30 ml) for 4 to 6 hrs. A solid separated on cooling was recrystallised from ethanol or benzene-petroleum ether (Table 1).

Acknowledgement

Grateful acknowledgements of the authors are due to Professor S.S. Tewari, Head, Chemistry Department, Lucknow University, Lucknow for providing departmental facilities and Dr. Nityanand, Director, CDRI, Lucknow for spectral data of the compounds. One of us (S.N.M.) is also thankful to the C.S.I.R., New Delhi for the award of J.R.F.

References

1. R. SPAUN, A. C. ROCHAT, J. J. GALLAY and P. BRENNEISEN, *Swiss Patent*, 540, 236, 1973 ; *Chem. Abs.*, 1974, **80**, 14764.
2. H. D. PORTER and H. M. TAYLOR, *Fr. Demande.*, 2, 169, 732, Oct. 19, 1973 ; *Chem. Abs.*, 1974, **80**, 82461.
3. V. L. NARAYANAN and R. D. HAUGWITZ, *U. S. Patent*, 3, 718, 662, 1973 ; *Chem. Abs.*, 1973, **78**, 136292.
4. G. D. DIANA (Sterling Drug. Inc.), *U. S. Patent*, 3, 790, 631, 1974 ; *Chem. Abs.*, 1974, **80**, 108219.
5. H. MARTIN, H. ARBI and L. EBNER, *U. S. Patent*, 3, 702, 368, 1972 ; *Chem. Abs.*, 1973, **78**, 25374.
6. J. J. GALLAY, R. BOSSHARD and P. BRENNEISEN, *Ger. offen.* 2, 259, 220, 1973 ; *Chem. Abs.*, 1973, **79**, 78781.
7. G. HOLAN and E. L. SAMUEL, *U. S. Patent*, 3, 520, 898, July 21, 1970 ; *Chem. Abs.*, 1970, **73**, 77234.
8. W. G. BYWATER, W. R. COLEMAN, OLIVER KAMM and H. HOUSTON MERRITT, *J. Amer. Chem. Soc.*, 1945, **67**, 905.

9. J. A. VAN ALLAN and B. D. DEACON, *Organic synthesis Coll. Vol. IV* (Ed) N. Rhobjon, p. 570.

10. G. I. BRAZ, (All. Union. Sci. Research Chem-Pharm. Ins. Moscow) *J. Gen. Chem. U.S.S.R.*, 1955, 25, 731-4 ; *Chem. Abs.*, 1956, **50**, 2457.

Chemical Examination of *Lindenbergia indica*

K. P. TIWARI* and R. N. CHOUDHARY

Department of Chemistry, University of Allahabad, Allahabad-211 002

Manuscript received 18 January 1979, accepted 4 March 1980

LINDENBERGIA indica (N. O. Scrophulariaceae) is an annual erect herb found throughout India. The juice of the plant is given in chronic bronchitis and mixed with that of coriander applied to skin eruptions[1,2]. No work has been reported in literature on this plant. A systematic chemical examination of *L. indica* was, therefore, undertaken and the results are reported in the present communication.

The air-dried powdered plant (2 kg) was extracted with petroleum ether (60-80°) in a Soxhlet extractor. The extract was concentrated to a small volume (200 ml) and kept in a refrigerator overnight whereby a yellow mass deposited. The deposit was filtered, washed with petroleum ether, taken in benzene and chromatographed over alumina. Elution with petroleum ether (40-60°) removed the waxy material. Further elution with petroleum ether : benzene mixture (7 : 3 v/v) gave a crystalline solid (800 mg) which when recrystallised from benzene afforded needles, m.p. 281°, $C_{30}H_{50}O$. It was characterised as friedelan-3-β-ol by spectral data[3,4] and by preparation of its acetate, m.p. 291° and benzoate, m.p. 198-9°.

The defatted plant material was then extracted exhaustively with ethanol. The ethanolic extract was concentrated under reduced pressure and the thick viscous mass so obtained was extracted with petroleum ether to remove any waxy material and chlorophyll. The residual mass was extracted with benzene and acetone successively. Benzene extract was concentrated and chromatographed over alumina. Elution with benzene and chloroform (7 : 3 v/v) mixture yielded a compound (670 mg) which when recrystallised from methanol-chloroform mixture afforded needles, m.p. 310°, $C_{30}H_{48}O_3$ (M^+, m/e 456) and characterised as oleanolic acid by comparison of its spectral data[3,4] and properties of its acetate methyl ester derivative and oxidised product[5].

The acetone extract was concentrated, dried and extracted with absolute ethanol. The ethanolic extract was concentrated to a syrup. Addition of excess of chloroform to the ethanolic syrup, precipitated a resinous mass. The resinous mass was separated by filteration. The filtrate was concentrated, dissolved in water and kept in a refrigerator for a week, whereby free flavone settled down at the bottom. It was separated and dissolved in a little of dried acetone, adsorbed over magnesol column and eluted with ethyl acetate saturated with water whereby a yellow compound was obtained. The compound on crystallisation from ethanol melted at 240° and identified as 7-hydroxy flavone by analysis, colour reactions, spectral data[6,7] and preparation of its derivatives. The filtrate obtained after separation of free flavone was extracted with ethylacetate for several times. The extract was concentrated and chromatographed over magnesol using ethyl acetate saturated with water as eluate, whereupon a yellow compound was obtained. The compound on crystallisation from methanol : ethanyl acetate mixture (1 : 1 v/v), melted at 185-7° and characterised as quercitrin by m.m.p. and superimposable IR spectrum with authentic sample.

Acknowledgement

One of us (R.N.C.) is obliged to C.S.I.R., New Delhi for the award of a J.R.F.

References

1. R. N. CHOPRA, S. L. NAYAR and I. C. CHOPRA, "Glossary of Indian Medicinal Plants", C. S. I. R., New Delhi, 1956, p. 154.
2. Wealth of India, C. S. I. R. Publication, New Delhi, 1962, Vol. VI, 59.
3. M. SHAMMA, R. E. GLICK and R. MUMMA, *J. Org. Chem.*, 1962, **18**, 1417.
4. C. DJERASSI, H. BUDZIKWICZ and J. M. WILSON, *Tetrahedron Lett.*, 1962, 263.
5. D. H. R. BARTON and P. D. MAYO, *J. Chem. Soc.*, 1954, 887.
6. L JURD and R. M. HOROWITZ, *J. Org. Chem.*, 1957, **22**, 1618.
7. T. J. BATTARHAM and R. J. HIGHET, *Aust. J. Chem.*, 1964, **17**, 428.

J. Indian Chem. Soc.,
Vol. LVII, April 1980, pp. 454

Book Review

Chromatography of polymers, Petroleum & Petrochemicals. Edited & Published by Sukumar Maiti of Materials Science Centre, IIT, Kharagpur.

This book is based on the papers presented at the Symposium and Workshop : Chromatography of Polymers, Petroleum and Petrochemicals held at IACS, Jadavpur, Calcutta-32 in December 1978.

There are 15 chapters altogether, each of which has been written by experts in the field of Chromatography. The book contains the basic principles of Gas Chromatography, Theory & Practice of GC, and its applications in the fields of (i) Polymer, (ii) Petroleum and (iii) Petrochemicals. It will be useful in the research laboratories of polymer, petroleum & petrochemicals.

The reviewer feels that the following facts should have been included :

(a) On page 15, it has been mentioned that "Gas tight pressurelock syringe is used for injection of gaseous samples". For precision quantitative work, the G. C. is hooked to a vacuum line via a 6-port stainless steel gas sampling valve. This eliminates totally the air peak from the chromatogram. The method has of course its limitations. The gas samples should not be absorbed/adsorbed by the O-rings of the sampling valve.

(b) Compounds should be identified by the use of multicolumns if the identification is made by the retention time or volume only, and not by a single column as suggested in the book. A single column may however be used if it is coupled with a MS or NMR, for identification of unknown chemical compounds.

(c) For quantitative estimation, peak height can be used if the peaks are very sharp, and provided the GC is calibrated accordingly. Hydrocarbons can be easily estimated quantitatively by this procedure if the sample is taken in a vacuum line which is connected to a GC by an automatic 6-port stainless steel gas sampling valve. Measurements of peak heights are also very easy, quick and accurate.

(d) On page 35, an alumina column has been recommended for the separation of H, air, Co, & short chain paraffins and olefins. In this column, normally silicone oil (1 to 2%) is used as a tail reducer for the peak. However, for continuous use, this column containing silicone oil will not be reliable as the silicone oil will gradually leave the column with the carrier gas, and more quickly if the temperature of the air thermostat is 80° or above. To overcome this difficulty, NaOH coated alumina is used as a stationary phase in the GSC.

R. S. Konar

AUTHOR INDEX

J. Indian Chem. Soc.,
Vol. LVII, May 1980, pp. 435-438

Studies on Metal Ammine Complexes—Part II. Polarographic Behaviour of Some Schiff Base Pentaammine Chromium(III) Complexes

W. U. MALIK, R. BEMBI, P. P. BHARGAVA, SUSHILA and O. P. TANDON

Department of Chemistry, University of Roorkee, Roorkee—247 672

Manuscript received 9 March 1979, revised 24 September 1979, accepted 4 March 1980

The polarographic behaviour of several newly synthesised chromium(III) complexes with Schiff bases has been described. The reduction waves in 0.1*M* LiCl corresponded to one electron reduction. These are diffusion controlled and irreversible in nature. The values of $k^{\circ}_{f,h}$ lie between 10^{-9} to 10^{-11} $cm^{-1}s^{-1}$. The irreversible behaviour may be interpreted in terms of 'Loosening' of the chromium(III) complex during reduction from Cr(III) to Cr(II). The complexes have been characterised by chemical analysis, conductance measurements and infrared spectra.

THE Schiff bases derived from amino acids are known to play an important role in biological reactions[1]. With an aim to elucidate the role of such Schiff bases as electron mediators, our previous studies[2-4] have now been extended to the complexes of the Schiff bases with pentaammine chromium(III) to gain further information on the problem. The results on the reduction of these complexes at the d.m.e. are presented in this communication.

Experimental

All reagents were AnalaR grade BDH products and their solutions were prepared in double distilled water. The organic solvents and salicylaldehyde were laboratory grade reagents. They were distilled twice prior to use.

Monochloropentaammine chromium(III) chloride was prepared by the method given Schlessinger[5]. The crude product was recrystallised from water and its spectra agreed with the literature values[6].

Two series of Schiff bases : (i) derived from aminoacids and (ii) derived from aminobenzoic acids were used. The Schiff bases of amino acids were prepared by the method of Dietrich as adopted by Martell[7] by condensing glycine(Gly), alanine(Ala), aspartic acid (S-A) and glutamic acid (G) with salicylaldehyde(S) and *o*-vanillin(V). The Schiff bases of amino benzoic acids were prepared by the method of Roe and Montgomery[8] by condensing *o*-aminobenzoic acid (OAB), *m*-aminobenzoic acid (MAB) and *p*-aminobenzoic acid (PAB) with benzaldehyde (B), salicyladehyde(S) and *o*-vanillin(V).

Preparation of the Complexes :

Complexes with Schiff bases derived from amino acids were prepared by warming to 50° for 30 min a solution containing 0.02 mole of the Schiff base and 0.01 mole of chloropentaammine chromium(III) chloride in 100 ml of water. After cooling to below 5°, 10 ml of 70% $HClO_4$ was added and the crude product washed first with alcohol and then with ether till free from $HClO_4$. After suspending in 100 ml of methanol, the product was stirred magnetically for 15 min and filtered off. The methanolic filtrate was concentrated to about 10 ml under vacuum at 40° and then cooled to below 5°. The desired complex was precipitated by adding 1:1 alcohol-ether mixture and recrystallised from 1*M* $HClO_4$ by adding ice cold 70% $HClO_4$. The pink product was washed thoroughly with alcohol till free from $HClO_4$ and then with ether and dried under vacuum over anhydrous calcium chloride.

Complexes of Schiff bases derived from amino benzoic acids were prepared by adding 0.1 mole of the Schiff base to 100 ml of a solution containing 2.4 g of chloropentaammine chromium(III) chloride and adjusting the *p*H to between 4-5 with Li_2CO_3. After heating at 50° for 30 min with magnetic stirring, the solution was cooled to room temperature and the insoluble material filtered off. The filtrate was cooled to about 2° in an ice bath and the complex precipitated by adding 10 ml of ice cold saturated $NaClO_4$. After standing in ice bath for 15 min, the precipitate was filtered off and washed with alcohol. The crude product was magnetically stirred for 30 min with 100 ml of methanol and filtered. The filtrate was concentrated under vacuum to about 10 ml and the desired complex precipitated by cooling in ice and adding ether. It was then recrystallised from 1*M* $HClO_4$ by adding 70% ice cold $HClO_4$, washed with alcohol, ether and dried under vacuum over anhydrous calcium chloride. The complexes with *o*-, *m*- and *p*-aminobenzoic acids were also prepared by the above method.

The complexes were subjected to chemical analysis for chromium, nitrogen and carbon. The complex was decomposed by prolonged heating with a strong

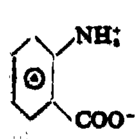
solution of NaOH and chromium estimated spectrophotometrically as chromate[9] after treating with hydrogen peroxide. These results were cross checked by estimating chromium with diphenyl carbazide[10] at 540 nm. Nitrogen and carbon were estimated at the Microanalytical Laboratories, Central Drug Research Institute, Lucknow (Table 1).

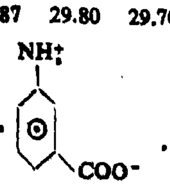
The molar conductance of the complexes was measured with a Systronics Conductivity Meter, Type 302, at 25 ± 0.1° using a dip type cell. The conductance was measured with a $1.0 \times 10^{-3} M$ solution of the complexes. The absorption spectra was recorded on a Carl-Zeiss, Specord, recording spectrophotometer. Infrared spectra was recorded on Beckmann IR-20 spectrophotometer in KBr by thin film technique.

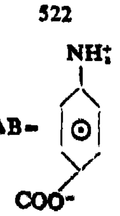
Polarograms were recorded on a Cambridge pen recording polarograph using a d.m.e. and saturated calomel electrode as reference electrode. The capillary

TABLE 1—CHEMICAL ANALYSIS, MOLAR CONDUCTANCE, VISIBLE AND INFRARED SPECTRAL DATA OF THE SCHIFF BASE SUBSTITUTED CHROMIUM(III) PENTAAMMINE COMPLEXES

Complex R=[Cr(NH$_3$)$_5$]	Chemical Analysis: Chromium % Found	Chromium % Calc.	Nitrogen % Found	Nitrogen % Calc.	Carbon % Found	Carbon % Calc.	Molar conductance at 25±.1°C ohm^{-1}cm^2	Wave-length of max. absorption λ_{max} ±1nm	Infrared absorption band at cm^{-1}: (COO$^-$) asy and NH$_3$ defor.	(COO$^-$) sym	(C=N)
1	2	3	4	5	6	7	8	9	10	11	12
[R-S-Gly](ClO$_4$)$_2$	10.00	10.11	16.40	16.34	23.45	23.34	260	525	1610	1415	1640
[R-S-Ala](ClO$_4$)$_2$	9.90	9.84	15.82	15.92	25.12	25.00	260	522	1610	1410	1650
[R-S-A](ClO$_4$)$_2$	9.15	9.09	14.70	14.66	25.02	25.17	255	522	1600	1410	1640
[R-S-G](ClO$_4$)$_2$	8.82	8.87	14.27	14.33	26.75	26.67	250	520	1600	1405	1640
[R-V-Gly](ClO$_4$)$_2$	9.62	9.55	15.49	15.44	24.21	24.26	255	527	1605	1410	1640
[R-V-Ala](ClO$_4$)$_2$	9.27	9.31	15.13	15.03	25.96	25.80	250	525	1610	1410	1650
[R-V-A](ClO$_4$)$_2$	8.52	8.63	13.82	13.95	25.78	25.91	245	524	1610	1410	1650
[R-V-G](ClO$_4$)$_2$	8.51	8.44	13.55	13.63	27.17	27.27	245	528	1610	1400	1640
[R-OAB](ClO$_4$)$_2$	9.00	9.08	14.50	14.67	14.80	14.67	350	517	1610	1400	–
[R-B-OAB](ClO$_4$)$_2$	9.22	9.28	14.90	15.00	30.08	30.00	245	520	1610	1390	1650
[R-S-OAB](ClO$_4$)$_2$	9.10	9.02	14.65	14.58	29.01	29.16	245	522	1605	1400	1640
[R-V-OAB](ClO$_4$)$_2$	8.64	8.58	13.92	13.87	29.60	29.70	240	522	1600	1400	1640
[R-MAB](ClO$_4$)$_2$	9.20	9.08	14.55	14.67	14.50	14.67	340	521	1605	1380	–
[R-B-MAB](ClO$_4$)$_2$	9.22	9.28	15.08	15.00	30.07	30.00	245	522	1605	1380	1650
[R-S-MAB](ClO$_4$)$_2$	9.06	9.02	14.52	14.58	29.25	29.16	250	525	1605	1380	1640
[R-V-MAB](ClO$_4$)$_2$	8.52	8.58	13.82	13.87	29.65	29.70	245	525	1605	1400	1650
[R-PAB](ClO$_4$)$_2$	9.15	9.08	14.55	14.67	14.78	14.67	345	520	1600	1385	–
[R-B-PAB](ClO$_4$)$_2$	9.20	9.28	15.06	15.00	29.95	30.00	240	521	1610	1380	1640
[R-S-PAB](ClO$_4$)$_2$	9.10	9.02	14.53	14.58	29.25	29.16	235	522	1605	1385	1640
[R-V-PAB](ClO$_4$)$_2$	8.50	8.58	13.80	13.87	29.80	29.70	235	522	1600	1400	1640

Note: OAB—


, MAB—


, PAB—


characteristic $m^{2/3} t^{1/6}$ was found to be 1.77 $mg^{2/3}$ $s^{-1/2}$. The temperature was maintained constant at 25° with a water thermostat. The polarograms were always recorded using freshly prepared solutions of the complexes in perchloric acid maintaining the *p*H at 3.0. The solutions were prepared by taking 1.0 to 7.0 ml solution of the complex (conc. about 0.01 *M*) and adding to them 0.4 ml of 0.1% gelatin and 1.0 ml of 1 *M* LiCl. The total volume was made upto 10 ml in each case with perchloric acid of *p*H 3.0.

Results and Discussion

Chemical analysis (Table 1) of the complexes confirms the formulae $[Cr(NH_3)_5SB](ClO_4)_2$ and $[Cr(NH_3)_5AB](ClO_4)_3$ where SB and AB represent the Schiff base and (*o*-, *m*- or *p*-) aminobenzoic acid respectively. Molar conductance values (Table 1) of the complexes lie in the range 235-260 and 340-350 respectively. The complexes gave λ_{max} in the range 517-539 nm.

The infrared spectra of the Schiff base pentaammine chromium(III) complexes show two bands around 1400 cm^{-1} and 1600 cm^{-1} (Table 1) which may be assigned to the symmetric and the asymmetric stretching of the carboxylic group[11,12]. In the case of complexes of the dicarboxylic acids (aspartic acid and glutamic acid), an additional band around 1700 cm^{-1} is observed which may be assigned to a free carboxyl group, indicating that in these complexes only one carboxyl group is involved in coordination. It is also observed that nitrogen of the C=N group of the Schiff base is not involved in complex formation since the band around 1640-1650 cm^{-1} present in the spectra of Schiff bases due to the C=N group does not show any shift. The complexes may then be represented as $[Cr(NH_3)_5OOCR](ClO_4)_2$.

In order to choose an appropriate supporting electrolyte, polarograms of the complexes were recorded using a number of supporting electrolytes. It was observed that well defined waves were obtained with 0.1*M* LiCl and 0.1*M* $NaClO_4$ as supporting electrolyte. The present studies were carried out in 0.1*M* LiCl. The complexes were found to undergo irreversible reduction. This is evident from the fact that the slope of the plots between log $\frac{i}{i_d - i}$ and E gave fractional values of n (of the order of 0.5) and $E_{1/2}$ show a shift with a change in concentration of the complex. The values of $i_d/h^{1/2}$ are constant indicating a diffusion controlled electrode process.

The diffusion coefficient, D, was evaluated with the help of Nernst Equation[13] :

$$D = \frac{RT}{ZF^2} \lambda_a \qquad \ldots \text{(a)}$$

where Z is the charge on the ion and λ_a is the equivalent conductance at infinite dilution. The ionic conductance of complex ion $[Cr(NH_3)_5SB]^{++}$ or $[Cr(NH_3)_5AB]^{+++}$ was calculated by subtracting the conductance value of the perchlorate ion (71 ohm^{-1} mol^{-1} at 25°) from the total conductance given in Table 1. The value obtained from this equation gives an approximate value of D because the molar conductance value used is for 0.01*M* solution rather than at infinite dilution. This approximate value of D when substituted in the Ilkovic equation enables one to calculate the value of n, the number of electrons involved in the electrode reaction. The values of n were calculated to be Ca 1.0, indicating a one electron transfer electrode process. The exact values of D (Table 2) were then evaluated from the Ilkovic equation using a value of n=1. Finally the values of D were used to calculate $K^0_{f,h}$, the formal rate constant for the electrode reaction, using the equation for an irreversible process[13-15].

TABLE 2—POLAROGRAPHIC DATA AT 25°C IN 0.1 *M* LITHIUM CHLORIDE IN PRESENCE OF 0.004% GELATIN FOR THE SCHIFF BASE SUBSTITUTED PENTAAMMINE CHROMIUM(III) PERCHLORATES.

Chromium(III) pentaammine complex with	$-E_{1/2}$ V (vs SCE)	αn	$D^{1/2} \times 10^3$ cm^2 sec^{-1}	$K^0_{f,h} \times 10^9$ cm^{-1} sec^{-1}
1	2	3	4	5
S-Gly	0.87	0.64	4.09	5.42
S-Ala	0.91	0.62	5.16	2.31
S-A	0.90	0.65	5.23	1.97
S-G	0.90	0.63	5.38	1.84
V-Gly	0.89	0.67	4.87	0.74
V-Ala	0.91	0.63	4.77	1.63
V-A	0.88	0.63	5.38	3.40
V-G	0.92	0.59	5.39	7.62
OAB	0.98	0.63	4.27	2.81
B-OAB	0.91	0.67	4.75	6.76
S-OAB	0.94	0.60	4.26	19.40
V-OAB	0.93	0.60	5.10	38.90
MAB	0.91	0.77	4.95	0.373
B-MAB	0.91	0.81	4.55	0.088
S-MAB	0.90	0.77	4.87	0.495
V-MAB	0.88	0.82	4.32	0.450
PAB	0.90	0.72	5.17	2.47
B-PAB	0.89	0.78	4.32	0.485
S-PAB	0.90	0.81	4.64	0.288
V-PAB	0.90	0.77	4.74	1.09

$$E_{d.e} + 0.2412 = \frac{0.05915}{\alpha n} \log \frac{1.349\ K^{\circ}_{f,h}}{D^{1/2}} - \frac{0.0542}{\alpha n}\left[\log \frac{i}{i_d - i} - 0.546 \log t\right]$$

A plot of $E_{d.e}$ versus $\left[\log \frac{i}{i_d - i} - 0.546 \log t\right]$ gives a slope equal to $\frac{0.0542}{\alpha n}$ and intercept equal to $\frac{0.05915}{\alpha n} \log \frac{1.349\ K^{\circ}_{f,h}}{D^{1/2}} - 0.2412$.

The values of $K^{\circ}_{f,h}$ (Table 2) lie in the range of 10^{-9} to 10^{-11} cm^{-1} sec^{-1} which further confirm the irreversible behaviour of the reduction waves. Since the reduction is a one electron transfer process the observed irreversible wave corresponds to the reduction of Cr(III) to Cr(II) and may be expressed as :

$$[Cr(NH_3)_5SB]^{2+} \xrightarrow{e^-} [Cr(NH_3)_5SB]^{+} \xrightarrow{5H^+} Cr(II) + 5NH_4^+ + SB$$

The irreversibility of the reduction step may be attributed to the change of configuration from $3d^2 4s\ 4p^3$ to $4s\ 4p^3 4d^2$. The 'loosening' of chromium(III) complex during the course of the reduction is in accord with the low rate of the electrode process. The $4s\ 4p^3 4d^2$ configuration for the Cr(II) complex has been demonstrated[16,17] for a Cr(II)-ethylene diamine complex which shows a magnetic moment of 4.4–4.5 B.M.

References

1. A. L. LEHNINGER, *Biochemistry*, Worth Publishers, New York, 1975.
2. W. U. MALIK, RAMESH BEMBI and SUSHILA, *J. Indian Chem. Soc.*, 1977, **54**, 762.
3. W. U. MALIK, RAMESH BEMBI and SUSHILA, *J. Indian Chem. Soc.*, (in press).
4. SUSHILA, Ph.D. Thesis, Roorkee University, Roorkee, 1977.
5. G. SCHLESSINGER, *Inorg. Syn.*, 1960, **6**, 138.
6. M. L. LEVINE, T. P. JONES, W. E. HARRIS and W. J. WALLACE, *J. Amer. Chem. Soc.*, 1961, **83**, 2453.
7. D. HEINERT and A. E. MARTELL, *J. Amer. Chem. Soc.*, 1962, **84**, 3257.
8. A. ROE and J. A. MONTGOMERY, *J. Amer. Chem. Soc.*, 1953, **75**, 910.
9. G. W. HAUPT *J. Res. Nat. Bur. Stand.*, 1952, **48**, 414.
10. A. I. VOGEL, '*Quantitative Inorg. Analysis*', Longmans, 1966.
11. D. N. SEN, Z. MIZUSHIMA, C. CURRAN and J. V. QUAGLIANO, *J. Amer. Chem. Soc.*, 1955, **77**, 211.
12. R. T. M. FRASER, *Inorg. Chem.*, 1964, **3**, 1561.
13. MEITES, '*Polarographic Techniques*', Interscience, New York, 1965.
14. KOUTECKY, *Coll. Czech. Chem. Comm.*, 1955, **18**, 597.
15. MEITES and ISRAEL, *J. Amer. Chem. Soc.*, 1961, **83**, 4903.
16. R. A. PLANE and H. TAUBE, *J. Phys. Chem.*, 1952, **56**, 33.
17. D. N. HUME and H. W. STONE, *J. Amer. Chem. Soc.*, 1941, **63**, 1200.

J. Indian Chem. Soc.,
Vol. LVII, May 1980, pp. 459-461

Schiff Base Complexes of Antimony(III) and (V) Chlorides

T. N. SRIVASTAVA, A. K. S. CHAUHAN and H. N. MEHROTRA

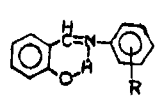
Chemistry Department, Lucknow University, Lucknow, India

Manuscript received 13 September 1978, accepted 9 February 1980

The direct interaction of antimony tri-and-pentachloride with salicylideneaniline and its amine ring substituted derivatives results in the formation of adducts with 1:1 stoichiometry. The newly synthesized compounds have been characterized through elemental analysis, conductance measurement and infrared data. It is concluded that the ligands coordinate to the metal atom through their azomethine nitrogen giving rise to four- and six-coordinated antimony complexes.

THE adduct-forming tendency of salicylideneanilines towards various transition and non-transition metal halides has been investigated[1-5]. Recently, Singh and Tandon[6,7] studied the reaction of antimony(III) isopropoxide with Schiff bases containing one o-OH group either in aldehyde or amine fragment and obtained chelates of 1:1, 1:2 and 1:3 stoichiometries where the bases in their anionic form behave as bidentate ligands.

The lewis acidity of both trivalent and pentavalent antimony chloride is well known[8] and molecular complexes with benzylideneanilines have been reported[9]. It was considered of interest to study the behaviour of these chlorides towards aromatic Schiff bases derived from salicylaldehyde in which the electron density at the azomethine nitrogen atom is disturbed owing to the formation of a quasi aromatic ring by intramolecular hydrogen bonding. The present communication reports the interaction of $SbCl_3$ and $SbCl_5$ with the following Schiff bases



$R=H(L-1)$; $p-CH_3(L-2)$;
$p-Cl(L-3)$;
$p-OCH_3(L-4)$;
$p-NO_2(L-5)$ and
$m-NO_2(L-6)$

Experimental

Anhydrous antimony trichloride (Albright and Wilson, UK) and pentachloride (Allied Chemicals, USA) were distilled under reduced pressure before use. The Schiff bases were prepared by the direct condensation of salicylaldehyde with aniline and its ring substituted derivatives in ethanol; the yellow to red compounds were recrystallized from the same solvent.

The molecular adducts were obtained by the direct interaction of antimony chlorides and Schiff bases in a dry inert solvent under nitrogen. In a typical experiment 5m moles (1.14 g) of $SbCl_3$ in 25 ml dry benzene were added dropwise to a solution of salicylideneaniline (4 g, more than 10 m moles) in the same solvent under stirring in an atmosphere of dry nitrogen. A sticky mass appeared almost instantaneously. The mixture was stirred for an hour to ensure complete precipitation and then refluxed on a water bath for 30 minutes which yielded a crystalline product. It was filtered, washed with the same solvent and dried in vacuum. The reactions of $SbCl_5$ were carried out in dichloromethane without refluxing.

The complexes were analysed for antimony. A weighed sample of the compound was decomposed with a mixture of conc. H_2SO_4 and HNO_3 and heated to remove nitric acid. The resulting antimony solution was reduced with sulphurous acid and Sb(III) precipitated as sulphide. The precipitate after filtration was dissolved in conc. HCl and titrated against a standard solution of potassium bromate[10]. The analytical data are reported in the table. The conductance measurements were made using a Phillips PR9500 conductivity bridge in nitrobenzene at 30°. The molar conductance values are listed in the table. The infrared spectra of the complexes were recorded using Perkin Elmer 157 spectrophotometer in KBr discs. The relevant frequencies along with their assignments are given.

Results and Discussion

All the complexes are intense yellow to red coloured solid, insoluble in common organic solvents excepting methanol and nitrobenzene and have sharp melting point. The analytical data show that the bases form adducts of 1:1 stoichiometry, in which they behave as neutral monodentate ligands coordinated to antimony atom irrespective of its oxidation state. Molar conductance values of the adducts suggest them to be non-electrolytes.

A critical comparison of the spectra of the free Schiff bases with those of the corresponding complexes, enables to draw certain conclusions concerning absorptions of diagnostic value. In the spectra of ligands the broad weak band centred around 2800 cm^{-1} is characteristic of intramolecularly H-bonded OH group[11]. On complexation this band is shifted

TABLE—EXPERIMENTAL DATA FOR $SbCl_3$ AND $SbCl_5$ ADDUCTS WITH THE SCHIFF BASES

Compound	m. p. °C	Elemental Analysis % Found (Calcd.) Sb	C	H	Molar Conductance (ohm^{-1} cm^2 $mole^{-1}$)	IR frequencies (cm^{-1})* ν(OH)	ν(C=N)
$SbCl_3$.L-1	155	29.02 (28.62)	37.14 (36.71)	2.58 (2.61)	6.25	2900mbr	1635m
$SbCl_3$.L-2	172	27.19 (27.71)	38.73 (38.27)	2.83 (2.98)	4.09	3000m	1640s
$SbCl_3$.L-3	181	26.79 (26.48)	33.54 (33.96)	2.30 (2.19)	3.12	2975m	1638s
$SbCl_3$.L-4	165	26.53 (26.74)	37.28 (36.93)	2.84 (2.88)	6.90	3025w	1642vs
$SbCl_3$.L-5	142	26.37 (25.89)	33.62 (33.20)	2.37 (2.14)	3.70	2950mbr	1640vs
$SbCl_3$.L-6	145	26.22 (25.89)	33.14 (33.20)	2.23 (2.14)	7.04	2950wbr	1635w
$SbCl_5$.L-1	180d	24.89 (24.53)	31.25 (31.46)	2.41 (2.23)	8.23	3100m	1637vs
$SbCl_5$.L-2	190	24.41 (23.86)	32.54 (32.95)	2.56 (2.57)	6.30	3090w	1638s
$SbCl_5$.L-3	208d	22.98 (22.94)	29.76 (29.42)	2.18 (1.90)	5.30	3125mbr	1635m
$SbCl_5$.L-4	170	23.57 (23.13)	31.67 (31.95)	2.37 (2.49)	5.83	3100m	1640vs
$SbCl_5$.L-5	198	22.83 (22.49)	29.15 (28.85)	1.97 (1.86)	3.15	3100w	1636vs
$SbCl_5$.L-6	195	22.91 (22.49)	29.29 (28.85)	2.07 (1.86)	5.72	3150w	1638m

* br=broad, m=medium, s=strong, v=very, w=weak.

to ~3000 and ~3100 cm^{-1} in adducts of $SbCl_3$ and $SbCl_5$ respectively. It is, therefore, inferred that the closed ring due to intramolecular H-bonding is retained in all the complexes in distorted form ; the extent of distortion being more in adducts of $SbCl_5$ than that in those of $SbCl_3$. This is in agreement with the earlier observations made by Tanaka *et al*[12]. Furthermore, the strong band appearing in the spectra of the ligands around 1280 cm^{-1} due to phenolic C-O stretching mode[19] shows negligible shift upon complexation and makes us believe that *o*-hydroxy group of the bases has not taken part in complex formation. The analytical data support the above conclusion.

The main indication of the formation of molecular complexes through infrared spectral data is an increase in the C=N stretching frequency, which suggests coordination of the Schiff bases through the nitrogen atom of the azomethine group. In accordance with the published data[14,15] stretching vibrations of the -CH=N- group in free salicylideneanilines are known to absorb in the range 1603-1622 cm^{-1}. In the spectra of the adduct studied here this band is shifted to 1638 ± 5 cm^{-1}. Similar observations are also reported for adducts of $TiCl_4$ and $SnCl_4$ with these bases[16]. The increase of νC=N during coordination may be due to the unshared pair of electrons at the nitrogen atom being attracted to the antimony atom, the n, π conjugation with the aniline ring is broken down and a partial positive charge is produced at the nitrogen atom. This hinders the usual π, π conjugation of the azomethine group with the aniline nucleus. The removal of the azomethine group from the conjugation and its electronic structure analogous to the structure of the protonated group $-CH=N^{+}H-$ increase the frequency of its aborption in the infrared spectra[2,17].

Acknowledgement

The authors are thankful to the Head of the Chemistry Department, Lucknow University, Lucknow for providing laboratory facilities and to the Director, Central Drug Research Institute, Lucknow for his help in collecting analytical and spectral data. Financial assistance from U.G.C., New Delhi, to A.K.S.C. and H. N. M. is gratefully acknowledged.

References

1. V. A. Kogan, O. A. Osipov, V. I. Minkin and V. P. Sokolov, *Russ. J. Inorg. Chem.*, 1965, 10, 45.
2. P. Bamfield, *J. Chem. Soc.*, A, 1967, 804.
3. S. S. Lyapina, V. V. Mishchenko, E. P. Trailina, I. A. Savich and V. I. Spitsyn, *Chem. Abs.*, 1970, 72, 116350e.
4. D. Negoiu, A. Kriza and M. Nasta, *Rev. Roum. Chim.*, 1974, 19, 1039.
5. K. Yamanouchi and S. Yamada, *Inorg. Chim. Acta*, 1974, 11, 223.
6. O. P. Singh and J. P. Tandon, *Indian J. Chem.*, 1976, 14A, 709.
7. O. P. Singh and J. P. Tandon, *Inorg. Chim. Acta*, 1976, 20, L37.
8. I. Lindquist, "Inorganic Adduct Molecules of Oxo-Compounds", Academic Press, New York, 1963.
9. L. A. Kuzitsyna, A. A. Nilson, N. B. Kupletskaya and O. A. Reutov, *Chem. Abs.*, 1966, 65, 11742e.
10. V. I. Vogel, "A Text Book of Quantitative Inorganic Analysis", Longsman, London, 1963, p. 385.
11. H. H. Freedman, *J. Amer. Chem. Soc.*, 1962, 83, 2900.
12. K. Kwakami, M. Miya-Uchi and T. Tanaka, *J. Inorg. Nuclear Chem.*, 1971, 33, 3773.
13. J. E. Kovacic, *Spectrochim. Acta*, 1967, 23A, 183.
14. T.N. Srivastava and A.K.S. Chauhan, *J. Inorg. Nuclear Chem.*, 1977, 39, 371.
15. G. C. Percy and D. A. Thornton, *J. Inorg. Nuclear Chem.*, 1972, 34, 3357.
16. L.J. Bellamy, "Infra-red spectra of complex Molecules", John Wiley and Sons, Inc., New York, 1954.
17. B. Witkol and T. W. Beiler, *J. Amer. Chem. Soc.*, 1954, 76, 5589.

J. Indian Chem. Soc.,
Vol. LVII, May 1980, pp. 462-465

Synthesis and Characterisation of Fe(III), Co(II), Ni(II) and Cu(II) Complexes with Schiff Base of 5-Phenylazosalicylideneaniline

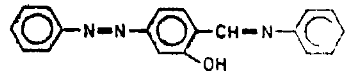
M. A. PUJAR* and T. D. BHARAMAGOUDAR

Department of Chemistry, Karnatak University Post-Graduate Centre, Gulbarga-585 105, India

Manuscript received 24 September 1979, accepted 30 December 1979

A new Schiff base ligand is synthesised by condensation of 5-phenylazosalicylaldehyde with aniline (PASA). The complexes of the type M(PASA) Cl. [M = Co(II), Ni(II) and Cu(II)] and Fe(PASA) Cl_2 have been prepared in the solid state and characterised by their elemental analysis, molar conductance, magnetic moments at room temperature and infrared spectral studies. The complexes are paramagnetic having subnormal magnetic moments, they may have MNON Cl chromophores instead of the expected MN_2O_2 group. The complexes are thought to possess either dimeric or linear polymeric structures.

THERE have been a number of studies of metal complexes of Schiff base ligands formed from salicylaldehyde or substituted salicylaldehydes with various aromatic amines[1-6]. But it is noted that, the Schiff base formed by condensation of 5-phenylazosalicylaldehyde with aniline did not receive attention in the field of structural chemistry, although few authors have first reported the metal complexes of 5-phenylazosalicylaldehyde[7,8]. It is therefore, thought by the present authors, that 5-phenylazosalicylidene aniline Schiff base would be an ideal ligand for synthesising it and for preparation of the metal complexes. In view of this, we present here the results of magnetic and infrared spectroscopic investigations of some new Fe(III), Co(II), Ni(II) and Cu(II) metal complexes of Schiff base ligand 5-phenylazosalicylidene aniline (I).



(I)

Experimental

Materials: The chemicals used in this investigation were of reagent grade. Salicylaldehyde and aniline were distilled before use.

Ligand: 5-Phenylazosalicylaldehyde (PAS) was prepared according to the method of Das and Trivedi[9]. Then the Schiff base was prepared by refluxing aniline with PAS in 1:1 molar ratio in alcoholic medium on water bath. The Schiff base 5-phenylazosalicylidene aniline (PASA) thus separated after cooling was then filtered and crystallised from alcohol (M. P. 140°).

Complexes: The metal complexes were prepared by treating the Schiff base dissolved in the least amount of ethanol with metal salts ($FeCl_3$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$ and $CuCl_2.2H_2O$) in molar ratio 1:1. The reaction mixture was refluxed for about 1 hr. The solution was then reduced to smaller volume on a water bath and after cooling pH was raised to 8 by 1:1 ammonia in alcohol. The respective solid complexes were filtered, washed with ethanol and dried in a desiccator over fused $CaCl_2$. The complexes were purified by soxhlet extraction.

Chemical Analysis: The solid ligand (PASA) obtained was analysed for carbon and hydrogen. The complexes were analysed for their metal and halogen by standard methods. The result of chemical analysis are recorded in Table 1.

Physical Measurements: The molar conductance of the complexes were made using ELICO (M-8) conductivity bridge with a cell having cell constant 0.829 cm^{-1}, manufactured by Electronic and Industrial Instrument Company, Hyderabad. The solutions were prepared in DMF and diluted to the required strength ($10^{-3}M$). The magnetic susceptibility measurements were made on a gouy balance at room temperature using $Hg[Co(SCN)_4]$ as calibrant. The i.r. spectra of the ligand and the complexes in nujol mull and KBr disc methods were recorded on Perkin Elmer 457 and 221 spectrometers in the 200-4000 cm^{-1} region.

Results and Discussion

The reaction of Fe(III), Co(II), Ni(II) and Cu(II) chlorides with Schiff base (PASA) gave only 1:1 complexes M(PASA)Cl[M = Co(II), Ni(II) and Cu(II)]

*For correspondence.

TABLE 1 – COLOR, M.P., CONDUCTIVITY, MAGNETIC MOMENTS AND ANALYTICAL DATA FOR Co(II), Ni(II), Cu(II) AND Fe(II) SCHIFF BASE COMPLEXES

Complex	M.P. °C. (Melts & decomposes)	Colour of the complexes	Metal %		Chlorine %		Conductivity ohm^{-1} cm^{2} mole^{-1}	μ_{eff} (B.M.)
			Found	Cal.	Found	Cal.		
Co(PASA)Cl	210	Light red	14.87	14.88	8.40	8.90	5.760	3.6
Ni(PASA)Cl	230	Yellowish green	14.55	14.86	8.50	8,96	2.173	2.9
Cu(PASA)Cl	290	Yellowish green	15.20	14.91	9.10	8.89	2.413	1.8
Fe(PASA)Cl_2	210	Darkish red	13.40	13.07	16.40	16.63	20.850	5.1
Ligand (PASA) $C_{19}H_{15}N_3O$	140	Red	Found : C=75.5%, H=4.84% Required : C=75.74%, H=4.94%.					

and Fe(PASA)Cl_2. The complexes can not be recrystallised from ethanol, because they were found to undergo thermal decomposition, when an attempt was made to recrystallise from hot solutions on account of low solubilities.

All the products are yellowish green to darkish red solids and are stable against light and atmosphere. They are soluble in polar solvents such as dimethyl formamide (DMF), pyridine etc. Practically all are insoluble in common organic solvents such as ethanol, acetone and benzene.

The molar conductance of these complexes in DMF at the concentration 10^{-3} M fall in the range 2—6 ohm^{-1} cm^{2} mole^{-1}. This value is too small to account for any dissociation of the complexes in DMF. Hence, these can be regarded as non-electrolytes in that solvent[10]. In case of Fe(III) complex, the value is 21 ohm^{-1} cm^{2} mole^{-1} and this may be due to the partial displacement of the chloro group by DMF in the coordination sphere of the complex.

The magnetic moments of the complexes calculated from the corrected magnetic susceptibilities determined at room temperature are given in Table 1. The magnetic moments μ_{eff} values reported for the complexes are lower than the spin-only value of respective metal ion complex[11]. The subnormal magnetic moments observed in the case of Fe(III), Co(II), Ni(II) and Cu(II) Schiff base complexes are accounted for by assuming dimeric or chain polymeric structures in the solid state and considerable interaction between metal ion systems owing to the spin-spin coupling, occurring antiferromagnetic interaction mechanism operating through the orbitals of metal ions[11-13]. These results may be accounted for by assuming predominantly dimeric or polymeric structures for these complexes.

TABLE 2 – SELECTED INFRARED ABSORPTION FREQUENCIES (cm^{-1}) OF PASA SCHIFF BASE LIGAND AND THEIR METAL COMPLEXES

Ligand	Fe(PASA)Cl_2	Co(PASA)Cl	Ni(PASA)Cl	Cu(PASA)Cl	Assignment
2700–2800brw	—	—	—	—	Intramolecular H bonded OH stretching
1625s	1620s	1610s	1615s	1615s	νC=N stretching
1590s 1580s 1570s	1525m	1535m	1530m	1525m	νN=N+νC=C aromatic stretching
1458vs	1385vs	1400vs	1406vs	1403vs	
1280s	1325brm	1322s	1330s	1345vs	Phenolic νC–O stretching
—	465brm	480brm	470m 482m	460m 470m	νM–N
—	370brm	365m 375m	365m 390m	350m 370w	νM–O

The selected infrared frequencies along with their tentative assignments are listed in Table 2. The broad and weak band with a fine structure in the region 2700-2800 cm^{-1} appearing in the spectra of the free ligand is attributed to the intramolecular hydrogen bonded OH established between the aldehydic *o*-OH group and the basic nitrogen atom. This assignment is in line with that made by other investigators[14-16]. The broad band of ligand disappears in the complexes leaving only a fine structure, which is due mainly to the CH modes.

In the PASA Schiff base, one can expect also stretching frequencies due to νC=N, νC=C and νN=N. Eventhough it has been reported that 5-phenylazosalicylaldehyde would show N=N stretching frequency around 1500 – 1575 cm^{-1} and 1460 – 1490 cm^{-1}[17]. It is however, difficult to assign the N=N stretching to the specific band in the aromatic azo compounds, because there is extensive coupling between νC=N, νC=C and νN=N modes. It is still more cumbersome in the Schiff base 5-phenylazosalicylidene aniline. Therefore the bands in the region 1460 – 1590 cm^{-1} are tentatively assigned to coupled ν(C=C) + ν(N=N) and these bands have remarkable change in their stretching frequencies on going from ligand to metal complex (Table 2).

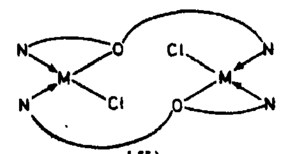
In the ligand spectrum the strong band appearing at 1625 cm^{-1} is assigned to νC=N stretching mode. In the metal complexes this band shifts to lower frequency region indicating that the coordination bond is formed between nitrogen of azomethine group and metal ion. This is in good agreement with previous assignment[6,16,20] for the νC=N mode in Schiff base complexes.

The strong band found around 1280 cm^{-1} in the ligand PASA Schiff base is assigned to the phenolic C – O stretching vibration[18]. This is shifted towards higher frequency on complexation. The higher frequency shift observed of the phenolic C – O bond in going from a hydrogen bonded structure to a covalent metal bonded structure, may be due to higher mesomeric interaction in the complex, which is activated by the presence of the metal ion[17].

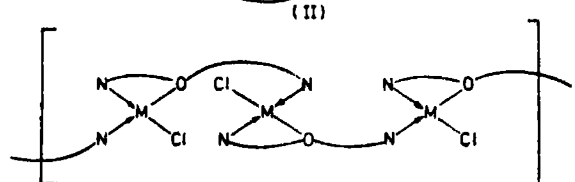
The metal-ligand, metal-oxygen, metal-nitrogen and metal-chloride vibrational modes are generally found to occur between 200 – 600 cm^{-1}. However, in these complexes, it is not easy to assign ν(M – N) and ν(M – O) vibrations, as the various skeletal vibrations of the ligand interfere with ν(M – N) and ν(M – O) vibrations. The assignments made are purely tentative and are based mainly on the information available in the literature.

Eventhough Nakamoto[18] reported that, no band in the structure of Schiff base complexes can be assigned to the ν(M – N) vibration, because of strong coupling between various modes. There are many other authors[19,20] who have assigned metal-nitrogen bands in the region 400 – 600 cm^{-1}. The medium and somewhat broad intense band found in the region 460 – 480 cm^{-1} (Table-2) attributed to ν(M – N) vibration. Taking into consideration of the observations of other authors[21,22] towards ν(M – O) assignment, medium intensity bands appearing in the region 350 – 370 cm^{-1} for these metal complexes are assigned to ν(M – O) vibration. Thus we have assigned ν(M – N) stretching modes to higher frequencies than ν(M – O) modes, as previous assignments on metal complexes containing "NO" ligands[23,24].

With the help of analytical data, conductivity, magnetic and infrared spectral data, it may be suggested that, all the metal ions have coordination number four in these complexes, except in Fe(III), where it is five. The construction of the models for the complexes indicates that, the monomeric structure involves much steric hindrance as the ligand molecule has to attach itself to one and the same metal ion through all its coordinating sites. The insolubility of the complexes in common solvents makes one to suggest a dimeric (II) or an extended polymeric structure (III). In view of these observations, we propose following structures for the complexes in which metal ions are maintained at the same coordination number.



(II)



(III)

Acknowledgement

The authors wish to thank Dr. C. N. R. Rao for providing facility to take infrared spectra and Dr. S. P. Hiremath, Head of the Department of Chemistry, Karnataka University, Post Graduate Centre, Gulbarga for encouragement. One of the authors (T.D.B.) is thankful to C. S. I. R. for providing a fellowship. We also thank Dr. V. H. Kulkarni for helpful discussions.

References

1. R. H. HOLM, G.W. EVERETTE, JR. and A. CHAKRAVORTY, *Prog. Inorg. Chem.*, 1966, 7, 83.
2. L. SACCONI, *Coord. Chem. Rev.*, 1966, 1, 126, 192.
3. M. AKBAR ALI and S. E. LIVINGSTONE, *Coord. Chem. Rev.*, 1970, 3, 101.
4. A. V. ABLOV, N. I. BELICHUK and L. N. NAZHELSKAYA, *Russ. J. Inorg. Chem.*, 1972, 17, 226.
5. M. D. HOBDAY and T. D. SMITH, *Coord. Chem. Rev.*, 1973, 9, 311.

6. V. H. Kulkarni, B. R. Patil and B. K. Prabhakar, *Mh. Chem.*, 1977, **108**, 1305.

7. K. G. Deshmukh and R. A. Bhobe, *J. Inorg. Nuclear Chem.*, 1978, **40**, 135.

8. H. Ohta, K. Nawata, C. Soejima and T. Tsumaki, *Mem. Fac. Sci. Kyushu, Univ. Ser.*, 1962, C 5, 1.

9. P. N. Mohan Das and C. P. Trivedi, *J. Indian Chem. Soc.*, 1972, **49**, 739.

10. W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.

11. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Wiley Eastern, New Delhi, 1972.

12. M. Kato, H. B. Jonassen and J. C. Fannino, *Chem. Rev.*, 1964, **64**, 99.

13. B. J. Halbert, C. M. Harris, E. Sinn and G. J. Sulton, *Aust. J. Chem.*, 1973, **26**, 951.

14. H. H. Freedman, *J. Amer. Chem. Soc.*, 1961, **83**, 2900.

15. V. H. Kulkarni and N. S. Biradar, *Rev. Roum. Chem.*, 1970, **15**, 1973.

16. J. E. Kovacic, *Spectrochim. Acta*, 1967, **23A**, 183.

17. M. R. Mahmoud, S. M. Issa, M. S. Elmelligy and S. A. Eloyar, *Mh. Chem.*, 1978, **169**, 861.

18. K. Nakamoto, "Spectroscopy and structure of metal-chelate compounds", (Ed.) K. Nakamoto and P. J. McCarthy, John Wiley, New York, 1968, p. 216.

19. J. R. Durig, B. R. Mitchell, D. W. Sink, J. N. Wills and A. S. Willson, *Spectrochim. Acta*, 1967, **23A**, 1121.

20. B. C. Sharma and C. C. Patel, *Indian J. Chem.*, 1970, **8**, 747.

21. G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, 1967, **6**, 433.

22. P. Gluvchinsky, G. M. Mockler and E. Sinn, *Spectrochim. Acta*, 1977, **33A**, 1073.

23. G.C. Percy, *Spectrochim, Acta*, 1976, **32A**, 1287.

24. J. R. Kincaid and K. Nakamoto, *Spectrochim. Acta*, 1976, **32A**, 277.

J. Indian Chem. Soc.,
Vol. LVII, May 1980, pp. 466-468

Formation and Reproportionation Constants of Mixed Ligand Complexes of Some Lanthanon Ions with Nitrilotriacetic Acid and β-isopropyltropolone

J. L. SHARMA, R. K. KADIAN, ISHWAR SINGH, B. S. GARG and R. P. SINGH

Department of Chemistry, University of Delhi, Delhi-110 007

Manuscript received 25 May 1979, accepted 4 March 1980

1:1:1 mixed ligand complexes of La(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III), Yb(III) and Y(III) with nitrilotriacetic acid and β-isopropyltropolone (βT) have been studied potentiometrically in 50% (v/v) aqueous dioxan medium at 0.1*M* $NaClO_4$ ionic concentration and 30±1°. The formation constants have been calculated by weighted least squares method. Reproportionation constant, which gives the idea about the compatibility of various ligands in the coordination sphere of a given metal ion, have also been calculated. The results of present investigation show that nitrilotriacetic acid and β-isopropyltropolone are incompatible ligands and the mixed ligand complexes are less stable than either of the parent complexes formed by the same ligands.

FORMATION and reproportionation constants of mixed ligand complexes of lanthanons using nitrilotriacetic acid (NTA) as primary ligand and tropolone as secondary ligand, have already been reported[1]. Mixed ligand complexes of bivalent metal ions with tropolones as secondary ligands while dipyridyl and phenanthroline as primary ligands have also been studied[2,3]. In the present communication, the results of potentiometric investigations on mixed ligand complexes of lanthanon ions using nitrilotriacetic acid (NTA) as primary ligand and β-isopropyltropolone (βT) as secondary ligand, have been discussed. The work has been extended to study the compatibility of these ligands in the coordination sphere of the metal ions and it has been observed that the stability of the mixed ligand complex formed is related to the stability of the binary complexes formed by same ligands.

Experimental

Apparatus and Reagents: A Beckman *p*H meter SS-2 model, with glass electrode and reference calomel electrode was used for *p*H-measurements. The gradual addition of alkali during titrations was done with the help of capillary nozzle. All metal ion solutions were prepared from A. R. lanthanon nitrate samples obtained from Indian Rare Earth Ltd. and their solutions were standardised by gravimetric method and complexometric method using xylenol orange as indicator. Nitrilotriacetic acid (Riedel) was dissolved in 3 equivalents of NaOH solution and was used as trisodium salt. β-Iso-propyltropolone (Koch-Light) was dissolved in freshly distilled dioxan, while tetramethyl ammonium hydroxide (TMAH) (E. Merck) was dissolved in 50% (v/V) aqueous dioxan and its solution was standardised against potassium hydrogen phthalate. Dioxan was purified by refluxing with sodium wire for 24 hours and was freshly distilled over sodium before use. All other chemicals used were of reagent grade. Presaturated nitrogen with (50% v/V aqueous dioxan) was passed through the solutions during titrations. The titration vessel was maintained at 30±1° with the help of thermostat. The following solutions (total volume 19.7 ml due to contraction in volume on mixing dioxan) were titrated against 0.05*M* TMAH solution.

(i) 3.0 ml $HClO_4$ (0.02*M*)+1.0 ml $NaClO_4$ (2.0*M*) +0.5ml $NaNO_3$ (0.02*M*)+5.5 ml water+10.0 ml dioxan.

(ii) 3.0 ml. $HClO_4$ (0.02*M*)+1.0 ml $NaClO_4$ (2.0*M*) +0.5 ml $NaNO_3$ (0.02*M*)+0.5 ml NTA (0.02*M*) +5.0 ml water +10.0 ml dioxan.

(iii) 3.0 ml $HClO_4$ (0.2*M*)+1.0 ml $NaClO_4$ (2.0*M*) +0.5 ml $NaNO_3$ (0.02*M*)+0.5 ml sec ligand (0.02*M*)+5.5 ml water+9.5 ml dioxan.

(iv) 3.0 ml $HClO_4$ (0.02*M*)+1.0 ml $NaClO_4$ (2.0*M*) +0.5 ml NTA (0.02*M*)+0.5 ml metal ion (0.02*M*)+5.0 ml water+10.0 ml dioxan.

(v) 3.0 ml $HClO_4$ (0.02*M*)+1.0 ml $NaClO_4$ (2.0*M*) +0.5 ml NTA (0.02*M*)+0.5 ml metal ion (0.02*M*)+0.5 ml sec ligand (0.02*M*)+5.0 ml water + 9.5 ml dioxan.

Results and Discussion

The proton ligand stability constant for βT and the formation constants for the following equilibria have been calculated as described in our earlier publication[1-4].

$$M + NTA \rightleftharpoons [M-NTA]$$

$$[M-NTA] + \beta T \rightleftharpoons [\beta T\text{-}M\text{-}NTA]$$

NTA reacts with lanthanon ions at lower *p*H which is evident from the titration curve of solution (iv). It has also been observed that titration curves for solutions (iv) and (v) overlap in lower *p*H range thereby showing that βT does not coordinate in this *p*H range. At higher *p*H (>4.5) the divergence of curves for solution (iv) and (v) shows the coordination of βT with the species [M-NTA]. Thus the formation constant of the mixed ligand complex may be given by

$$\beta_{1,1} = \frac{[\beta T\text{-}M\text{-}NTA]}{[M\text{-}NTA]\,[\beta T]}$$

The formation constants for NTA and βT binary complexes have been redetermined under present set of conditions and are in good agreement with earlier reported values[5]. $\bar{n}$ and pL values have been calculated by the method of Irving and Rossotti[6] and these values have been utilized for the computation of formation constants by weighted least squares method[7]. The β_n values were first approximated from ($\bar{n}$, pL) data with weight factor being unity. Second approximations to the β_n values were then calculated by attaching to them appropriate weight factors, computed from first set of β_n values. This process was repeated till successive cycles produced a change of less than one part per thousand in each β_n values. The consistency of the resulting parameters, measurements and the esteemed errors associated with measurements are tested by calculating the values of S_{min}, which have the same significance as χ^2, with k degrees of freedom[8].

Reproportionation constant (K_d) correlates the relative stability of mixed ligand complex with those of the parent complexes formed using same ligands. The correlation between the formation constants and reproportionation constant is given by the following relation :

$$K_d = \frac{\beta_{j,i}}{\beta_{m,0}^{j/m} \cdot \beta_{0,m}^{i/m}} \quad \text{(where } i+j=m\text{)}$$

According to this equation, formation constant of the mixed ligand complex is directly proportional to the geometric mean of the formation constants of the parent complexes and the proportionality factor is reproportionation constant. Reproportionation constant gives the measure of the compatibility of different ligands in the coordination sphere of a given metal ion. If the ligands are incompatible, then the mixed ligand complex formed will be less stable than either of the parent complexes and the reproportionation constant will be less than one[9]. Results of these investigations are listed in Table 3.

TABLE 1—FORMATION CONSTANTS OF BINARY COMPLEXES OF LANTHANONS WITH β-ISOPROPYLTROPOLONE AT 30±1°, CALCULATED BY BJERRUM'S HALF INTEGRAL METHOD

Metal ion	log K_1	log K_2	log β_2	log K_3	log β_3
H^+	7.92	–	–	–	–
La(III)	7.46	6.04	13.50	3.82	17.32
Pr(III)	7.54	6.31	13.85	4.68	18.53
Nd(III)	7.64	6.60	14.24	5.08	19.32
Sm(III)	7.78	7.22	15.00	5.62	20.62
Gd(III)	7.74	6.75	14.49	5.05	19.54
Dy(III)	7.90	7.58	15.48	6.08	21.56
Yb(III)	8.20	7.75	15.95	6.53	22.48
Y(III)	7.85	7.43	15.28	5.95	21.23

TABLE 2—FORMATION CONSTANTS OF BINARY COMPLEXES OF LANTHANONS WITH β-ISOPROPYLTROPOLONE AT 30±1°, CALCULATED BY WEIGHTED LEAST SQUARES METHOD

Metal ion	log K_1	log K_2	log β_2	log K_3	log β_3	S_{min}
La(III)	7.12	5.82	12.94	3.85	15.79	0.1286
Pr(III)	7.28	5.98	13.26	4.51	17.77	0.0015
Nd(III)	7.42	6.10	13.52	4.51	18.03	0.0186
Sm(III)	7.53	6.18	13.71	4.65	18.36	0.0211
Gd(III)	7.48	6.20	13.68	5.10	18.78	0.0176
Dy(III)	7.64	6.29	13.93	5.40	19.33	0.0158
Yb(III)	7.85	6.32	14.17	5.58	19.75	0.1215
Y(III)	7.70	6.29	13.97	5.31	19.30	0.1007

TABLE 3—FORMATION AND REPROPORTIONATION CONSTANTS OF MIXED LIGAND COMPLEXES OF LANTHANONS WITH β-ISOPROPYLTROPOLONE AND NITRILOTRIACETIC ACID AT 30±1°

Metal ion	β_{11}	S_{min}	K_d
La(III)	1.26×10^5	0.524	6.20×10^{-11}
Pr(III)	2.75×10^5	0.229	2.04×10^{-11}
Nd(III)	7.41×10^5	0.027	1.72×10^{-11}
Sm(III)	1.23×10^6	0.056	0.94×10^{-11}
Gd(III)	2.04×10^6	0.125	1.17×10^{-11}
Dy(III)	3.71×10^6	0.090	1.06×10^{-11}
Yb(III)	6.92×10^6	1.897	0.76×10^{-11}
Y(III)	2.57×10^6	0.203	0.35×10^{-11}

Present investigations reveal that :

(i) mixed ligand complexes are less stable than either of the parent complexes formed by the same ligands. Although the entropy effect always favours the formation of mixed ligand complex, but the steric hindrance created by bulky NTA molecule for the incoming βT anion, reduces the stability of the mixed species considerably. Also, the electrostatic force of attraction between [M-NTA] and βT should be less than that of βT with $[M(H_2O)_n]^{3+}$.

(ii) The values of $\beta_{1,1}$ for the mixed ligand complexes are found to be greater than $\beta_{0,2}$ for binary complexes. It is quite evident, because in the formation of ML_2 species with NTA the coulombic repulsion forces are greater. The formation of species $[\beta T\text{-}M\text{-}NTA]^-$ is always preferred over the formation of $[M\text{-}(NTA)_2]^{3-}$ or $[M\text{-}(\beta T)_2]^+$.

(iii) The formation constants of mixed ligand complexes of tropolone[1] have lower values as compared to those formed by β-isopropyltropolone using NTA as primary ligand. This is in good agreement with the pK values of these ligands.

(iv) The values of reproportionation constant is less than one in all the cases. This shows that NTA and βT are incompatible ligands in the coordination sphere of lanthanon ions. Also, these values are quite close to one another (Table 3), which indicates that all the lanthanon ions behave in the same manner towards these two ligands. This may be due to the differences in the structures and the bond types of the parent complexes formed by these two ligands[10,11]. In such cases, the bond between the metal ion and one of the ligands become more ionic and that between the metal ion and the other ligand becomes more covalent. These effects are of opposite sign and the net energy change may be either positive or negative depending upon the nature of species involved[12].

(v) The parallel change in the reproportionation constants and formation constants is not general. In the present studies also, it has been noticed that reproportionation constant does not vary linearly with formation constants. Although, the value of formation constant increases from lanthanum to ytterbium but at the same time the value of reproportionation constant decreases in disordered manner. In general, it can be concluded that these values depend upon the number, nature of the coordinating ligands and their mutual interactions present in the coordination sphere of the given metal ion. At the same time, the properties of metal ion such as ionic radii, also have their major role in deciding the compatibility of the ligands.

References

1. J. L. Sharma, B. S. Garg and R. P. Singh, *Monatshifte Chemie*, 1978, **109**, 847.
2. J. L. Sharma, B. S. Garg and R. P. Singh, *J. Inorg. Nuclear Chem.* 1980, **42**, 399.
3. J. L. Sharma, J. N. Srivastava, B. S. Garg and R. P. Singh, *Curr. Sci.*, 1977, **46**, 103.
4. J. L. Sharma, Ishwar Singh, B. S. Garg and R. P. Singh, *J. Indian Chem. Soc.*, 1978, **55**, 542.
5. Stability constants of metal ion complexes, compiled by A. E. Martell, Society Burlington House, London, 1964.
6. H. M. Irving and H. S. Rossotti, *J. Chem. Soc.*, 1954, 2904.
7. J. C. Sullivan, J. Rydberg and W. F. Miller, *Acta Chem. Scand.*, 1959, **13**, 2023.
8. J. Rydberg and J. C. Sullivan, *Acta Chem. Scand.*, 1959, **13**, 2059.
9. Ya. D. Fridman, *Proc. 3rd Symp. Coord. Chem. Budapest (Hungary)*, 1971, **II**, 78.
10. S. Kida. *Bull. Chem. Soc. (Japan)*, 1960, **33**, 1365.
11. S. Kida, *Bull. Chem. Soc. (Japan)*, 1961, **34**, 962.
12. S. Bruchenstein and C. D. Pitit, *J. Amer. Chem. Soc.*, 1966, **88**, 4790.

J. Indian Chem. Soc.,
Vol. LVII, May 1980, pp. 469-470

Formation Constants of Al(III), Cr(III) and Fe(III) Complexes with Some Substituted Salicylaldehydes

V. G. RATOLIKAR

Department of Chemistry, Institute of Science, Nagpur-440 001

Manuscript received 16 July 1979, accepted 30 December 1979

Formation constants of complexes of salicylaldehydes and its derivatives with Al(III), Cr(III) and Fe(III) have been determined at 30° in dioxane-water (75% v/v) medium containing 0.1*M* $NaClO_4$ using Calvin-Bjerrum technique as modified by Irving and Rossotti. The relation between log K_1^H and log K has been investigated.

IN continuation of our earlier studies[1] on the determination of formation constants of Cu(II), Ni(II), Co(II), Zn(II) and Mn(II) chelates with substituted salicylaldehydes, the formation constants of Al(III), Cr(III) and Fe(III) chelates with salicylaldehyde, 3-chloro, 4-hydroxy, 5-iodo, 6-chloro and 3-nitro-5-methyl substituted salicylaldehydes as well as with 2-hydroxy-1-naphthaldehyde[2] have been determined. The data reported in this work are in 75% (v/v) dioxane-water medium at an ionic strength 0.1*M* ($NaClO_4$) and 30°±0.1°.

Experimental

All the reagents used were of AR grade. Salicylaldehyde was obtained from Bush (Germany) and 4-hydroxysalicylaldehyde and 2-hydroxy-1-naphthaldehyde from B.D.H. (England). The details of preparations of remaining substituted salicylaldehydes, metal perchlorates and purification of dioxane are given in previous publication[1].

The procedure employed to carry out potentiometric titrations, the description of *p*H meter used, the calculations of $\bar{n}_A$, $\bar{n}$, pK and log K values were the same as given in earlier communication.

Results and Discussion

For the chelates of substituted salicylaldehydes with Al(III), Cr(III) and Fe(III) ions, the highest value of $\bar{n}$ is 2.6, thereby indicating conclusively the formation of 1:1, 1:2 and 1:3 complexes. From $\bar{n}$ values, it was seen that in these systems 1:1, 1:2 and 1:3 complexation occurs in short range of B(*p*H) values. The increase in $\bar{n}$ values is continuous for Al(III) and Cr(III) complexes while in the case of Fe(III) complexes, it is surprisingly high. Precipitation was obtained at B = 5.2 for Al(III), and B = 5.8 for Cr(III) ions, while in the case of Fe(III) it occurred at B=2.8 – 3.0.

The values of log K_1, log K_2 and log K_3 for these complexes are given in Table 1 along with the reported

TABLE—1 pK AND LOG K VALUES

Sl. No.	Ligand	pK	Al(III)			Cr(III)			Fe(III)		
			log K_1	log K_2	log K_3	log K_1	log K_2	log K_3	log K_1	log K_2	log K_3
1.	Salicylaldehyde	10.15	9.26	9.05	8.76	9.95	8.03	7.58	10.63	10.15	10.12
2.	3-Chloro-salicylaldehyde	8.55	7.94	—	—	8.46	6.79	—	—	9.08	9.34
3.	4-Hydroxy salicylaldehyde	12.91 9.14	12.61	12.02	11.71	13.07	11.45	10.68	—	13.33	13.24
4.	5-Iodo-salicylaldehyde	8.98	8.77	8.27	8.18	9.14	7.68	7.08	9.49	9.62	9.20
5.	6-Chloro-salicylaldehyde	9.65	8.70	8.49	7.90	9.04	7.46	—	10.54	10.20	9.48
6.	3-Nitro-5-methyl salicylaldehyde	6.48	—	—	—	7.04	5.23	—	—	7.41	7.20
7.	2-Hydroxy-1-naphthaldehyde	6.77	8.56	8.05	6.92	8.70	7.20	—	—	9.57	7.85

values of pK of substituted salicylaldehydes[1]. For Fe(III) complexes, the values of log K_3 were approximately evaluated due to non availability of more n̄ values in the expected range and even this made impossible the calculation of log K_1 values in most of the systems. The differences in the values of log K_1 and log K_2 and log K_3 are less than unity for Al(III) and Fe(III) complexes while in the case of Cr(III) complexes it is higher than one excepting for 5-iodo complexes. In general, the differences in the values of log K_1 and log K_2, and log K_2 and log K_3 are of such magnitude that it leads to infer that complexation 1:1, 1:2 and 1:3 might be occurring simultaneously.

The increase in the values of stability constants with decrease in ionic radii was observed in the case of Cr(III) and Fe(III) complexes. However, the stability of Al(III) complexes is more than these complexes. Similar observations have been reported by Banks and Singh[3] in relation to Al(III)-5 sulfosalicylate complexes.

Log K=apK+b relation :

The plot of log K_1 vs pK for Al(III) complexes is linear with unit slope value. The points relating to 5-iodo and 4-hydroxy salicylaldehyde are, however, not on the straight line which indicates extra π-bonding stabilization. Even plots of log K_2 and log K_3 vs pK are found linear with slope values 1.30 and 1.46 respectively.

The plots of log K_1 and log K_2 vs pK in relation to Cr(III) complexes are linear with slope values 1.63 and 0.85 respectively while in the case of Fe(III) complexes only plot of log K_2 vs pK is seen linear with slope value 0.98.

Fe(III) forms stronger complexes with substituted derivatives of salicylaldehyde than the complexes of Cr(III) and Al(III). This has been confirmed by the formation curves.

References

1. V. G. Ratolikar, D. V. Jahagirdar and D.D. Khanolkar, *Indian J. Chem.*, 1978, **16A**, 510.

2. V.G. Ratolikar, *J. Inorg. Nuclear Chem.*, 1979, **41**, 250.

3. C. V. Banks and R. S. Singh, *J. Inorg. Nuclear Chem.*, 1960, **28**, 125.

J. Indian Chem. Soc.,
Vol. LVII, May 1980, pp. 471-474

Co(II), Ni(II) and Cu(II) Complexes of Dopamine and Isoprenaline

B. L. VIJAYVARGIYA, P. B. CHAKRAWARTI* and H. N. SHARMA†

Chemical Laboratories, Govt. Girls College, T. T. Nagar, Bhopal-462 005

Manuscript received 23 August 1979, accepted 30 December 1979

Conductometric and spectrophotometric studies indicate formation of (M:L) 1:1 and 1:2 complexes between Co(II), Ni(II), Cu(II) and the two ligands Dopamine and Isoprenaline. The stepwise and the overall stability constants have been calculated and the thermodynamic parameters, ΔG, ΔH and ΔS, have been worked out at three temperatures 0°, 25° and 37° and a fixed ionic strength of 0.1*M* with KCl. The order of stability was found to vary as Cu(II) > Ni(II) ≃ Co(II). Structures of the complexes isolated have also been proposed on the basis of the analytical data and IR spectra.

CATECHOL amines include important drugs used as vasopressors, bronchodilators, circulatory stimulants and local vasoconstrictors. Many normal and transition elements are found to form complexes with phenol and phenolic amines[1]. Noradrenaline and Adrenaline complexes of many transition elements have been reported[2-8] in the literature. In the present communication is reported a study of the complexes of Co(II), Ni(II) and Cu(II) with Dopamine and Isoprenaline.

Experimental

High purity grade chemicals were used. Cu(II), Co(II) and Ni(II) chlorides were of A. R. (BDH) grade. Stock solutions were prepared in double distilled water and were standardised by standard methods. Dopamine hydrochloride (Rhein, Germany) and Isoprenaline (Burroughs Wellcom Ltd., India) were dissolved in deionised boiled water. 1 ml of 2*N* HCl/100 ml solution for the experimental solution was added to check the hydrolysis.

Stoichiometry: Stoichiometry of the complexes formed was ascertained by spectrophotometric and conductometric studies.

The spectrophotometric measurements were carried out with "Spekol" (Carl Zena Zessis, Germany) using the cells of the length 5 cm. The solutions of the ligands and the metal salts were diluted to required concentrations and mixed in the metal : ligand ratio of 2:1, 1:1 and 1:2 and the absorbance was noted at different wavelengths.

Absorbance suggested a single maxima at 355 mμ for all the three Dopamine-metal systems; while for Isoprenaline-Cu(II) and Co(II) systems λ_{max} was found to be at 410 mμ and 350 mμ respectively. Job's method of continuous variation[9] (applied with two concentrations 0.0004 *M* and 0.0005 *M*) indicated formation of 1:2 (M:L) complexes with these ligands and the metals.

The conductometric studies were carried out with the Toshniwal Conductivity Bridge using dip-type conductivity cell (having a cell constant 0.42). 10 ml of the ligand solution (0.01 *M*) was diluted to 100 ml and was titrated with 0.01 *M* metal solution. The conductances were recorded after each addition of 0.5 ml of the metal solution and were corrected to the dilution effect. The plots of conductance vs volume of the metal added indicated formation of two 1:1 and 1:2 (M:L) complexes with these metals and the ligands.

Stability and Thermodynamic constants:

Calvin-Bjerrum's method[10] as adopted by Irving and Rossotti[11] has been utilised to calculate stepwise and the overall "Formation constants" at three temperatures 0°, 25° and 37° and at a fixed ionic strength of 0.1 *M* with KCl. The experimental procedure consists in titration of the following thermostated mixtures of solutions with a 0.2 *M* alkali solution and recording the *p*H reading after each addition of 0.05 ml of the alkali:

(i) Mixture (A) : 5 ml of (0.002 *M*) HCl solution.

(ii) Mixture (B) : Mixture (A) + 10 ml of (0.001 *M*) Ligand (Dopamine or Isoprenaline)

(iii) Mixture (C) : Mixture (B) + 5 ml of (0.005 *M*) metal solution.

The ionic strength of the above solutions was maintained to 0.1 *M* by adding the required quantity of 1.0 *M* KCl solution, keeping the total volume 50 ml with double distilled water.

*M. L. B. College, Bhopal, to whom correspondence is to be made.
†M. V. M., Ujjain.

TABLE 1—STABILITY CONSTANTS, DOPAMINE COMPLEXES—$\mu = 0.1\ M$ (KCl)

S.No.	Metal ion	Temp. 0°C	log K_1	log K_2	log $K_1.K_2$	log β_2 (Overall)
1.	Cu(II)	0	9.500 (10.78)	1.000 (4.67)	15.500 (15.47)	15.200 (15.48)
		25	9.100 (9.79)	5.800 (4.43)	14.900 (14.22)	14.800 (14.24)
		37	8.100 (10.40)	5.250 (3.73)	13.350 (14.13)	13.100 (14.14)
2.	Ni(II)	0	6.123 (7.0)	3.650 (2.288)	9.773 (9.88)	9.400 (9.90)
		25	5.273 (6.60)	3.440 (2.26)	8.713 (8.86)	8.600 (8.86)
		37	4.580 (6.20)	3.350 (2.20)	7.930 (8.40)	7.700 (8.40)
3.	Co(II)	0	5.620 (6.41)	3.5 (2.70)	9.12 (9.11)	8.90 (9.12)
		25	5.150 (6.17)	3.15 (2.00)	8.30 (8.17)	8.10 (8.16)
		37	4.550 (5.52)	3.0 (1.81)	7.55 (7.33)	7.04 (7.34)

Note : Values given in the parenthesis are those obtained by Least Square Method.

TABLE 2—STABILITY CONSTANTS, ISOPRENALINE COMPLEXES—$\mu = 0.1\ M$ (KCl)

S.No.	Metal ion	Temp. 0°C	Log K_1	Log K_2	log $K_1.K_2$	Log β_2 (Overall)
1.	Cu(II)	0	9.5 (11.05)	8.0 (6.29)	17.5 (17.34)	17.3 (17.34)
		25	9.45 (11.0)	7.2 (6.10)	16.65 (17.10)	16.5 (17.10)
		37	8.95 (10.59)	6.232 (4.71)	15.182 (15.30)	15.0 (15.30)
2.	Ni(II)	0	5.95 (6.64)	3.25 (2.64)	9.2 (9.48)	8.5 (9.48)
		25	5.7 (6.61)	3.2 (2.56)	8.9 (9.17)	8.2 (9.16)
		37	5.375 (6.38)	3.05 (2.21)	8.425 (8.59)	7.8 (8.58)
3.	Co(II)	0	5.2 (6.15)	3.0 (2.31)	8.2 (8.46)	8.0 (8.46)
		25	5.05 (6.11)	2.95 (2.14)	8.0 (8.25)	7.72 (8.26)
		37	4.90 (6.08)	2.8 (2.08)	7.70 (8.16)	7.30 (8.16)

Note : Values given in parenthesis are those obtained by the Least Square Method.

The values of $\bar{n}$H, $\bar{n}$ and pL were calculated using the Irving-Rossotti equations[11] and the values of log K_1, log K_2, log $K_1.K_2$ and log β_2 were recorded directly from the formation curves. The refined values for the same were computed by the best least square fits (Table 1 and 2).

The thermodynamic parameters computed for the complexation reactions studied in this investigation are free energy, enthalpy and entropy changes and have been calculated using the isotherm, the isobar and the Gibbs-Helmholtz's equations respectively at 25° and 37° and at a ionic strength of 0.1 *M* with KCl (Table 3).

A perusal of the Table 1 to 4 indicates the order of stability to vary as : Cu(II) > Ni(II) ≈ Co(II), while that of $\triangle$H as : Ni(II) > Cu(II) > Co(II). Andrews *et al*[3] have studied the stability of Cu(II), Ni(II) and Co(II) complexes with Adrenaline and Noradrenaline. A comparison of the same with that obtained in the present investigation using Dopamine and Isoprenaline is given in Table 4, which clearly indicates that stability of the complexes with the ligands having secondary amino group is greater than that having primary amino group : (Isoprenaline > Dopamine, cf. Adrenaline > Noradrenaline).

Isolation and Composition :

Isolation of the complexes was done by refluxing equimolar solutions of the metal and the ligand in Metal : Ligand 1:2 ratio (Ligand in the slight excess than the stoichiometric ratio) for 5 hours. The solution was then concentrated to one fifth of the original volume on a water bath. The complex was then separated by vacuum drying in a vacuum dessicator. The excess of the ligand was removed by washing with absolute alcohol in which the complex dissolves leaving behind the uncomplexed ligand. The alcoholic solution is then dried under vacuum and pure complex was obtained. The composition of the different complexes has been ascertained by estimating the metal[12], nitrogen by semimicro Kjeldahl method[13] and the quantity of water associated.

The physical properties of the complexes-isolated and their analytical data are recorded in Table 5. Based on the analytical data the composition of the complexes was found to be ML_2 with Cu(II) and Ni(II) and $ML_2.2H_2O$ with Co(II).

IR Spectra :

The important IR frequencies (along with their assignments) recorded on Perkin Elmer infrared spectrophotometer, Model 237, for the complexes isolated indicate considerable change in the characteristic frequencies of – OH group in all the complexes of the ligands and hence the complexation may be considered to take through the phenolic hydroxyl groups, forming a five membered ring as suggested by Andrews *et al*[3] Further the potentiometric (*p*H) titrations indicated

TABLE 3—DATA ON STEPWISE AND OVERALL ENERGY OF FORMATION, LIGATIONAL ENTHALPIES AND LIGATIONAL ENTROPIES OF COMPLEXES

Metal ion	Temp. 0°C	$-\Delta G_1$	$-\Delta G_2'$	$-\Delta G_2$ (Overall)	$-\Delta H_1$	$-\Delta H'_2$	$-\Delta H_2$ (Overall)	ΔS_1	ΔS_2	ΔS_2 (Overall)
Cu(II)	0° DA	11.942	7.542	19.106	—	—	—	—	—	—
	IP	11.942	10.056	21.746	—	—	—	—	—	—
	25° DA	12.494	7.963	20.320	5.955	2.978	5.955	21.943	16.728	48.205
	IP	12.975	9.886	22.655	0.744	11.910	11.910	41.043	6.792	36.057
	37° DA	11.567	7.497	18.707	14.65	7.848	21.974	−9.945	−1.178	−10.539
	IP	12.781	8.899	21.420	5.755	18.500	24.067	22.665	30.971	−8.539
Ni(II)	0° DA	9.675	4.588	11.816	—	—	—	—	—	—
	IP	7.479	4.085	10.685	—	—	—	—	—	—
	25° DA	7.240	4.723	11.808	12.655	3.126	11.190	−18.171	5.359	2.074
	IP	7.826	4.394	11.259	3.722	0.744	4.466	13.772	12.248	22.795
	37° DA	6.54	4.784	10.996	15.146	3.139	17.789	−27.761	5.359	2.074
	IP	7.676	4.355	11.138	6.017	2.093	7.325	5.352	7.297	12.300
Co(II)	0° DA	7.064	4.40	11.187	—	—	—	—	—	—
	IP	6.536	3.771	10.056	—	—	—	—	—	—
	25° DA	7.071	4.325	11.121	6.997	5.211	11.910	0.248	−2.973	−2.648
	IP	6.934	4.050	10.60	2.233	0.744	4.169	15.775	11.094	21.580
	37° DA	6.497	4.284	10.053	11.196	5.232	19.463	−15.158	−3.058	−30.355
	IP	6.997	3.998	10.424	3.139	2.093	7.325	12.445	6.145	9.997

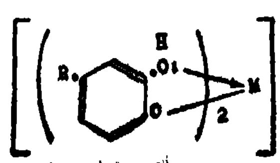
DA = Dopamine ; IP = Isoprenaline.

TABLE 4—COMPARISON OF STABILITY CONSTANTS—$\mu = 0.1\ M$ (KCl)

Metal ion	Temperature	log K_1			
		Ad[2]	Na[2]	DA	IP
Cu(II)	0°	10.96	10.25	9.50	9.50
	25°	10.50	9.13	9.10	9.45
Ni(II)	0°	6.17	5.76	6.123	5.95
	25°	5.62	5.28	5.273	5.70
Co(II)	0°	6.09	5.32	5.62	5.20
	25°	5.42	4.82	5.15	5.05

Ad = Adrenaline
NA = Noradrenaline
DA = Dopamine
IP = Isoprenaline

liberation of only one proton during the complexation of each molecule of the ligand. Hence, considering the coordination numbers of the metals, Cu(II) and Ni(II)=4 and Co(II)=6, and the analytical data the following general structures may be proposed for the complexes studied in this investigation :



R = $CH_2.CH_2.NH_2$ in Dopamine

= $CH(OH).CH_2.NH.CH(CH_3)_2$ in Isoprenaline.

M = Co(II), Ni(II) or Cu(II).

The remaining coordination positions in Co(II) complexes are filled with two H_2O moles. This finds

TABLE 5—PHYSICAL PROPERTIES AND THE ANALYTICAL DATA

Complex	Properties	% Metal		% N		% H_2O	
		T	F	T	F	T	F
1. $Cu(C_8H_{10}O_3N_2)$	Dark Brown powder, hygroscopic, highly soluble in H_2O and alcohol, m.p. 186°.	17.279	17.135	07.619	7.523	–	–
2. $Co(C_8H_{10}O_3N)_2 2H_2O$	Pinkish Red, crystalline, nonhygroscopic, soluble in H_2O and alcohol, m.p. 192°.	14.774	14.576	7.019	7.001	9.024	8.992
3. $Ni(C_8H_{10}O_3N)_2$	Bluish Violet, crystalline, non-hygroscopic, soluble in water and alcohol, m.p. 189°.	16.184	16.004	7.72	7.810	–	–
4. $Cu(C_{11}H_{16}O_3N)_2$	Dark Brown, hygroscopic, highly soluble in water and alcohol, m.p. 195°.	13.133	13.10	5.791	5.659	–	–
5. $Co(C_{11}H_{16}O_3N)_2 2H_2O$	Bluish Violet, hygroscopic, highly soluble in H_2O and alcohol, m.p. 172°.	11.446	11.506	5.437	5.321	6.991	6.973
6. $Ni(C_{11}H_{16}O_3N)_2$	Greenish Brown, hygroscopic, highly soluble in H_2O and alcohol, m.p. 186°.	12.262	12.14	5.849	5.792	–	–

confirmation in the presence of the bands at frequencies 3600 – 3200 and 880 – 650 in IR spectra of the Co(II) complexes studied here.

References

1. YOKITA MURAKAMI, KATSUYUKI NAKAMURA and MASASUKE TOKUNAKA, *Bull. Chem. Soc. Japan*, 1963, 36(6), 669.
2. A. C. ANDREWS, T. D. LYONS and T. D. O. BRIEN, *J. Chem. Soc.*, 1962, 1776.
3. JACCO HALMEKOSKI, *Soum. Kemistrilehti.*, 1962, 35, 209.
4. R. F. JAMESON and W. F. S. NEILLEI, *J. Inorg. Nuclear Chem.*, 1966, 31 (12), 3809.
5. JACCO HALMEKOSKI, *Seum. Kemistrilehti*, 1962, B-35, 238.
6. T. D. SMITH, S. G. CARR and J. R. PILBROW, *J. Chem. Soc.*, A16, 1971, 2569.
7. I. MURO, I. MORISHIMA and T. YONEZAWA, *Chem. Biol. Interactions*, 1971, 3(3), 213.
8. S. SINISTRI, L. VILLA and V. FERRI, *Pharmacol. Ed. Sci.*, 23(2), 210.
9. P. JOB, *Ann. Chim. Scand.*, 1928, 10(9), 133.
10. J. BJERRUM, '*Metal amine formation in aqueous solutions*' P. Haase and Sons, Copenhagen, 1967.
11. I. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.*, 1953, 3397 and 1954, 2904.
12. I. VOGEL, '*Quantitative Inorganic Analysis*' Longmans Green & Co. Ltd., 3rd Edn. 1961.
13. MOHAMMAD ASHRAF, *Talanta*, 1968, 15, 559.

J. Indian Chem. Soc.,
Vol. LVII, May 1980, pp. 475-477

The Nature and Composition of the Complexes of Mo(VI) with Halogen Substituted Ortho-Hydroxy Acetophenone Oxime

H. SINGH, U. K. RATHI* and N. SINGH**

Chemical Laboratories, D. S. College, Aligarh, Aligarh-202 001

Manuscript received 23 July 1979, accepted 29 December 1979

The complexes of molybdenum(VI) with 2-hydroxy-5-chloro and 2-hydroxy-5-bromo acetophenone oximes have been studied spectrophotometrically in water-ethanol medium. The yellow coloured solid complexes of above ligands were isolated by refluxing the metal and ligand solutions in stoichiometric ratio. These complexes were characterized by analytical, thermal, infra-red spectral and magnetic susceptibility data. The composition of above complexes comes out to be 1:2 (metal:ligand), the general formula being $MoO_2(C_8H_7O_2NX)_2$; where X=Cl and Br. The IR spectral study of complexes show that these ligands act as bidentate ligand with molybdenum(VI) and coordination takes place by formation of M-O and M←N bonds through the oxygen of phenolic group and nitrogen of oxime group with metal. The magnetic susceptibility data reveals that complexes are diamagnetic, octahedral in nature and molecular weights determined by cryoscopic method show the monomer character. The stability constants are 5.5×10^8 and 2.31×10^8 ; and free energy of formation $\Delta F°$ are -12.11 and -11.59 K cal/mol in case of 2-hydroxy-5-chloro acetophenone oxime and 2-hydroxy-5-bromo acetophenone oxime respectively, determined spectrophotometrically applying the Mole-Ratio method.

THE reagents containing the system $-\overset{\text{OH}}{\overset{|}{C}}=\overset{|}{C}-\overset{|}{C}=NOH$ are very good complexing agents. Therefore, salicylaldoxime[1-3], resacetophenone oxime[4], ortho-hydroxy acetophenone oxime and its derivatives[5-6] etc have been used. The present communication deals with the spectrophotometric, conductometric, thermal and spectral study of Mo(VI) complexes employing 2-hydroxy-5-chloro acetophenone oxime (HCAOX) and 2-hydroxy-5-bromo acetophenone oxime (HBAOX).

Experimental

Preparation of reagents : 2-Hydroxy-5-chloro acetophenone and 2-hydroxy-5-bromo acetophenone were prepared almost quantitatively by Fries migration[8] of *p*-chlorophenyl acetate and *p*-bromophenyl acetate respectively. The corresponding oximes (HCAOX) and (HBAOX) prepared by usual methods were crystallised in ethanol, HBAOX (m.p.169°) and HCAOX (m.p.181°).

Ammonium molybdate solution : The standard solution[9] of ammonium molybdate (J. T. Baker) was prepared by dissolving the salts in double distilled water. Ammonium acetate and acetic acid were used to maintain the *p*H.

A "spectronic-20" spectrophotometer was used for the measurement of optical density. The conductometric titrations were done with the help of Toshniwal conductometer and IR spectra was recorded on Perkin-Elmer spectrophotometer.

Spectrophotometric Study :

Absorption curve : Vosburgh and Coopers[9] method was employed to determine the nature and number of complexes present. The formation of yellow coloured complexes take place in water-ethanol medium of Molybdenum(VI) with both ligands (HCAOX-HBAOX). The maximum absorption occurs at 385 nm only which suggests the formation of one complex with each ligand.

Effect of pH, time and addition of reagents : The yellow colour complex of Mo(VI) takes place in the *p*H range 2 to 5.5 but the maximum colour intensity was observed at *p*H 4.5 with both ligands. There is no change in colour intensity up to a week and sequence of reagent addition got no significant effect on optical density.

Composition of the complex : Jobs method of continuous variation[10], mole ratio[11] and slope ratio[12] methods were employed to determine the stoichiometry (metal : ligand) of the complex. The results of these methods showed the 1 : 2 composition.

*To whom all correspondence should be made.

**Present address : Chemistry Department, Hindu College, Moradabad.

The stability constants of complexes in case of both ligands were determined by mole-ratio method using the following expression

$$K = \frac{1-\alpha}{4.C^2.\ \alpha^3}$$

$$\text{where } \alpha = \frac{Em - Es}{Em}$$

C is the concentration of complex and α is the degree of dissociation. The terms Em and Es having their usual meanings.

The stability constants obtained from above method are 5.5×10^8 and 2.31×10^8, and the free energy of formation, calculated from the relation $\triangle F^0 = RT$ ln K, are-12.11 and-11.59 K cal/mol for the complexes of both ligands (HCAOX) and (HBAOX) respectively.

Conductometric titrations :

The direct and indirect titrations and Jobs method by conductometry also reveal the same 1 : 2 (metal : ligand) stoichiometry of these complexes.

Isolation of solid complexes :

The stoichiometric mixtures of metal solution and ligand in water-ethanol 30 : 70 (v/v) was refluxed on water bath for six hours and cooled. A bright yellow coloured complex deposited in case of both ligands were washed with water and ethanol and then dried in vacuum. These complexes were crystallized in ethanol. The chemical analyses of these complexes is in confirmity with the composition of mole ratio 1:2.

The elemental analyses showed the following results :

Complex	C%	H%	N%	Mo%	
$MoO_2(C_8H_7O_2NCl)_2$	38.58	2.78	5.61	19.20	(Found)
	38.65	2.81	5.63	19.29	(Calcd.)
$MoO_2(C_8H_7O_2NBr)_2$	33.80	2.38	4.80	16.62	(Found)
	32.76	2.56	4.77	16.37	(Calcd.)

Thermal analysis :

The molybdenum-HCAOX and molybdenum-HBAOX chelates are thermally stable up to 160°. This indicates that the complexes are not hydrated. TGA curves of the metal complexes showed a rapid loss in weight in which the ligands carbon residue is almost completely lost is 200 to 500°. In the end, the residue of MoO_3 is left behind.

Spectral studies :

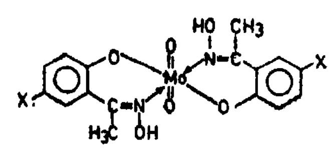
The infra-red spectra recorded in Nujol-Mul of ligands and complexes. The ligands show the strong absorption bands of phenolic groups but no such bands are obtained in complexes. The disappearance of this band clearly points out to the replacement of phenolic hydrogen by the metal. The C=N frequency is also lowered in the complex. The lowering in C=N frequency and replacement of phenolic hydrogen atom clearly indicates that chelation takes place through the oxygen of –OH group and nitrogen of =NOH group. Some main frequencies are tabulized here below :

Compound	OH (phenolic) cm^{-1}	–C=N cm^{-1}	–NO– cm^{-1}
$C_8H_8O_2NCl$	3300	1585	1280
$MoO_2(C_8H_7O_2NCl)_2$	–	1570	1265
$C_8H_8O_2NBr$	3350	1590	1240
$MoO_2(C_8H_7O_2NBr)_2$	–	1560	1230

Result and Discussion

The molar conductivity determined in dioxane shows the non-electrolytic behaviour of the complexes and the molecular weights determined by cryoscopic method reveal that these complexes are monomer in nature. The magnetic study of these complexes claims the octahedraldiamagnetic character.

On the basis of above results, the structure of the complex can be depicted as :



(X = Cl and Br)

Acknowledgement

Author's have manyfold indebtedness to Dr. S. S. Gupta, Principal, D.S. College, Aligarh-202 001, for his moral support and UGC for financial assistance. One of the authors (U. K. Rathi) is grateful to Agra University, Agra for the award of UGC Junior Research Fellowship.

References

1. F. Ephraim, *Ber.*, 1930, **63B**, 1928.
2. J. H. Flagg and N. H. Furman, *Ind. Eng. Chem. Anal. Ed.*, 1940, **12**, 529.
3. M. Jean, *Bull. Soc. Chim.*, 1943, **10**, 201.
4. K. S. Bhatki and M. B. Kabadi, *J. Sci. Ind. Res.*, 1952, **11B**, 346 ; *J. Univ. Bombay*, 1955, **24**, 51.
5. S. N. Poddar, *Z. Anal. Chem.*, 1957, **154**, 254 ; 1957, **155**, 327.
6. S. Prakash, Y. Dutt and R. P. Singh, *Indian J. Chem.*, 1968, **6**, 664.
7. A. I. Vogel, "Quantitative Inorganic Analysis", Longmans Green & Co. Ltd., London, 2nd edition, 1960, p. 506.
8. K. Fries, *Ber.*, 1908, **41**, 427.
9. W. C. Vosburgh and G. R. Cooper, *J. Amer. Chem. Soc.*, 1942, **64**, 1630.
10. P. Job, *Annals. Chem.*, 1928, **9(10)**, 113.
11. Yoe and Jones, *Ind. Eng. Chem. Anal. Edn.*, 1944, **16**, 111.
12. Harvey and Manning, *J. Amer. Chem. Soc.*, 1950, **72**, 4488.

J. Indian Chem. Soc.,
Vol. LVII, May 1980, pp. 478-480

Cu^{+2}, Ni^{+2} and Co^{+2} Chelates of N-N′-Hexamethylene-*bis* (2:5:di-OH, Acetophenone/ Propiophenone/Benzophenone)

R. B. PATEL and J. K. VERMA

Govt. College, Daman

and

R. K. SEVAK

Arts, Science and Commerce College, Kholwad

Manuscript received 21 August 1979, accepted 22 December 1979

The Schiff bases N-N′-hexamethylene *bis*-(2:5:di-OH, acetophenone, propiophenone and benzophenone) are used to study their complex forming behaviour with the copper(II), nickel(II) and cobalt(II) ions. Elemental, molecular weight determination, conductivity, magnetic moments and electronic spectra were carried out to assign a square plannar structure for copper(II), nickel(II) and cobalt(II) chelates.

The I.R. spectra shows the characteristic stretching vibrations of $\bar{\nu}$ (M-N) and $\bar{\nu}$ (M-O) below 500 cm^{-1}.

MUCH research work is being done now a days on metal chelates of Schiff bases[1(a),(b)]. The present paper reports the study of the complex forming behaviour of the following Schiff bases with the ions copper(II), nickel(II) and cobalt(II)

(i) N-N′-hexamethylene-*bis* (2 : 5 : di-OH-acetophenone)

(ii) N-N′-hexamethylene-*bis* (2 : 5 : di-OH-propiophenone)

(iii) N-N′-hexamethylene-*bis* (2 : 5 : di-OH-benzophenone)

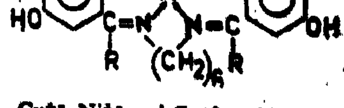
Experimental

(a) *Preparation of Schiff bases* : The two moles of 2 : 5 : di-OH-acetophenone, 2 : 5 : di-OH-propiophenone and 2 : 5 : di-OH-benzophenone and one mole of hexamethylene diamine were refluxed in presence of absolute alcohol on water for thirty minutes. The yellow-brown precipitates of all the three Schiff bases formed were filtered and washed with 50% alcohol to remove unreacted ketones and finally they were dried and recrystallised from chloroform giving m.p. 189°, 130° and 169° respectively.

(b) *Preparation of Chelates* : The solid Schiff bases and buffered metal ions solutions of copper, nickel and cobalt were refluxed on water bath for two hours. The cobalt(II) chelates of all the three Schiff bases were prepared by passing hydrogen gas during the preparation of these chelates. The reddish brown, yellowish brown and reddish black precipitates of copper(II), nickel(II) and cobalt(II) respectively formed were filtered and washed with water to remove excess of metal ions and then with 50% absolute alcohol to remove excess of Schiff bases. They were dried at room temperature. Because of less solubility in chloroform, benzene etc, they were not recrystallised. They are soluble only in D.M.F.

(c) *Analytical* : All the nine chelates were decomposed by perchloric acid and the estimation of metal ions were carried out by standard methods[2,3]. The molecular weights determined cryscopically using Camphor as a solvent showed monomeric in nature[4]. The conductivity of all the chelates was determined in D.M.F. on 'Toshniwal Conductivity Bridge' proving their non-electrolytic nature[5]. The percentage of nitrogen in each case was estimated by Kjeldahls method. The results of several such determinations are present in Table 1

The structure of all the three divalent metal chelates can be depicted as shown below :



Where M = Cu^{+2}, Ni^{+2} and Co^{+2} and R = $-CH_3 \rightarrow H_2SB_1$
$-C_2H_5 \rightarrow H_2SB_2$ $-C_6H_5 \rightarrow H_2SB_3$

TABLE 1

No.	Name of chelates	Molecular formula	Mol. Weight Exp.	Mol. Weight Found	% of Metal Exp.	% of Metal Found	% of Nitrogen Exp.	% of Nitrogen Found	Conductivity mhos cm²/mole	Magnetic moment in B.M. μ_{eff}	λ	ϵ
1.	$CuSB_1$	$C_{22}H_{26}O_4N_2$ – Cu	445.54	440	14.27	14.90	6.28	6 45	10	1.80	640 565 390	(108) (230) (5800)
2.	$CuSB_2$	$C_{24}H_{30}O_4N_2$ – Cu	473.54	490	13.43	12.89	5.91	5.78	10	1.84	630 570 390	(105) (172) (5600)
3.	$CuSB_3$	$C_{32}H_{30}O_4N_2$ – Cu	569.54	580	11.16	11.86	4.91	4.70	12	1.78	630 570 385	(102) (170) (5500)
4.	$NiSB_1$	$C_{22}H_{26}O_4N_2$ – Ni	440.71	425	13.32	12.68	6.35	6.55	5	dia	590 515 405	(410) (1050) (4700)
5.	$NiSB_2$	$C_{24}H_{30}O_4N_2$ – Ni	468.71	480	12.52	13.10	5.97	5.80	10	dia	590 510 410	(420) (1040) (4700)
6.	$NiSB_3$	$C_{32}H_{30}O_4N_2$ – Ni	564.71	540	10.40	10.89	4.96	4.72	5	dia	585 510 410	(410) (1060) (4800)
7.	$CoSB_1$	$C_{22}H_{26}O_4N_2$ – Co	440.94	435	13.38	13.98	6.35	6.18	10	1.89	660 510 400	(300) (2500) (7100)
8.	$CoSB_2$	$C_{24}H_{30}O_4N_2$ – Co	468.94	490	12.57	11.82	5.97	5.76	15	1.92	670 510 400	(290) (2500) (6700)
9.	$CoSB_3$	$C_{32}H_{30}O_4N_2$ – Co	564.94	550	10.45	10.90	4.96	4.82	10	1.93	670 500 390	(264) (2880) (7800)

(d) *Magnetism* : The magnetic susceptibilities of all the chelates were determined on a Gouy balance at room temperature. The copper chelates show one unpaired electron as the magnetic moment $\mu_{eff} = \sim 1.8$ B.M. on the basis of a square planar structure[6,7]. The nickel chelates are found to be diamagnetic having zero unpaired electron on the basis of square planar structure[6,7]. The cobalt chelates show one unpaired electron as the magnetic moment $\mu_{eff} = \sim 1.9$ B.M. on the basis of square planar[6,7] structure. The square planar cobalt(II) chelates show higher magnetic moment than the value ~ 1.7 B.M. expected on the basis of a spin only formula $\mu_{eff} = \sqrt{n(n+2)}$ B.M. for one unpaired electron due to orbital contribution which is due to mixing $^2A_{2g}$ into $^2A_{1g}$. The value ~ 1.9 B.M. is consistant with a square planar[6,7] structure.

(e) *Electronic Spectra* : The electronic spectra of all the chelates were recorded on 'Spectronic-20'. The solvent used was chloroform. The copper chelates show the following bands

640 nm (ϵ = 108)
565 nm (ϵ = 230)
390 nm (ϵ = 5800)

These may be assigned on an idealised D_{4h} symmetry to the following transitions.

640 nm $^2A_{1g} \leftarrow {}^2B_{1g}$
565 nm $^2Eg \leftarrow {}^2B_{1g}$

The band at $\sim$390 nm is quite intense and seems to be a charge transfer band. The nickel chelates show the following bands

590 nm (ϵ = 410)
515 nm (ϵ = 1050)
405 nm (ϵ = 4700)

The first two bands $\sim$590 nm and $\sim$515 nm could be due to the electronic transitions $^1B_{1g} \leftarrow {}^1A_{1g}$ and $^1E_g \leftarrow {}^1A_{1g}$.

The band at ~405 nm could be an intraligand band. The cobalt chelates show the following bands

660 nm (ϵ= 300)
510 nm (ϵ=2500)
400 nm (ϵ= 7100)

The first two bands at ~660 nm and ~510 nm could be due to the transitions

$^2B_{1g} \leftarrow ^2A_{1g}$ and

$^2E_g \leftarrow ^2A_{1g}$

The band at ~400 nm could be a characteristic of charge transfer band.

(f) *I. R. Spectra*: The I. R. Spectra reveal the M-N and M-O stretching vibrations[8] at ~480 and ~420 cm^{-1} respectively. The rest of the frequencies fit very well with the depicted structure.

References

1. (a) R. H. HOLM, G. W. EVERETT, JR. and A. CHAKRAVARTY cited in "Progress in Inorganic Chemistry" Edited by F. A. Cotton Vol. (VII) p. 83: Inter Science Publication 1966 and references therein.

(b) B. O. WEST, cited in "New Pathways in Inorganic Chemistry" edited by EAV. Eds. worth, A. G. MADDOCK and A. G. SHARPE, p. 303, Cambridge University Press, 1968 and references therein.

2. CUMMING and KEY "Quantitative Analysis", Ed. Robert Alexander Chalmers (Oliver and Boyd Publishers, London) 1956, p. 257.

3. A. I. VOGEL, "Quantitative Inorganic Analysis" (Longman), 1969, p. 526.

4. A. I. VOGEL, A Text Book of Practical Organic Chemistry (including qualitative organic analysis) Third Ed. Longman, 1961, p. 1037.

5. A. P. AMES and P. G. SEARS, *J Phys. Chem. Ithaca*, 1955, 59, 16.

6. W. A. EARNSHAW, Introduction to Magnetio Chemistry (Academic Press, New York), 1968, p. 35.

7. B. N. FIGGIS, "Introduction to Ligand Fields" (Wiley) 1966, 318.

8. KAZUO NAKAMOTO "Infrared Spectra of Inorganic and Co-ordination Compounds", John Wiley and Sons, New York, 1963, p. 146, 162, 422.

J. Indian Chem. Soc.,
Vol. LVII, May 1980, pp. 481-484

Complexes of Nickel(II) and Copper(II) with *p*-Aectamido Benzaldehyde Thiosemicarbazone

C. B. MAHTO

Department of Chemistry, Gopalganj College Gopalgan

Manuscript received 2 November 1979, accepted 22 December 1979

The complex compounds of nickel(II) and copper(II) with *p*-acetamido benzaldehyde thiosemicarbazone ($CH_3-CO-NH-C_6H_4-CH=N-NH-CS-NH_2$), (Abbreviated as *p* abts) of the type (ML_2)SO_4 and (ML_2) have been prepared and characterised. The structures of these complexes have been established on the basis of their elemental analysis, ir. uv and magnetic moment values. The nickel(II)-complexes were found to be diamagnetic and square planar. The copper(II)-complexes were found to be paramagnetic and their structures contributed more towards the planar ones.

p-Acetamidobenzaldehyde thiosemicarbazone is a well known antitubercular drug. Crim and others[1] have shown recently the importance of the metal chelates against cancer. This attracted the author's attention to prepare the *p*-acetamidobenzaldehyde thiosemicarbazone complexes of nickel(II) and copper(II) of which uptill now there is no mention in literature. The complexes have been characterised and their structures have been established with a view to add something new to the medicinal science, which will show, on test, whether these have actually got any anti diseases activity.

Materials: $NiSO_4 6H_2O$(E.M.), $CuSO_4.5H_2O$(E.M.) and $C_{10}H_{12}OSN_4$ were employed in the present work.

Ligand solution:

0.02(*M*) Solution of ligand either in ethyl alcohol or 0.1 (*M*) NaOH solution was used.

Standard solution:

0.04(*M*) solutions of Ni(II) and Cu(II) were made and reserved.

Complexes: [M(*p*abts)$_2$]SO_4:

Each of Ni(II) and Cu(II) solutions, was treated with ethanolic solution of the ligand in 1:2 molar ratio. In actual practice, to 20 cc of each of 0.04 (*M*) Ni(II) and Cu(II) solutions, 40 cc of 0.02 (*M*) ethanolic solution of the ligand were added and heated on water bath for more than an hour. Yellow coloured crystaline complexes formed were filtered, washed and dried in air.

Analytical data:

Found: Ni, 9.33; C, 38.26; H, 3.80; S, 15.27 and N, 17.83 percent.

For [Ni(*p*abts)$_2$]SO_4, Calculated: Ni, 9.36; C, 38.29; H, 3.82; S, 15.31 and N, 17.87 percent.

Found: Cu, 10.00; C, 37.93; H, 3.78; S, 15.15 and N, 17.70 percent.

For [Cu(*p*abts)$_2$]SO_4, Calculated: Cu, 10.05; C, 38.00; H, 3.80; S, 15.20 and N, 17.73 percent.

M(*p*abts)$_2$: 30 cc of each of 0.04 (*M*) Ni(II) and Cu(II) solutions were treated in cold with a slight excess of 0.02 (*M*) ligand solution in 0.1(*M*) NaOH. Greenish yellow precipitate of Ni(*p*abts)$_2$ was formed at *p*H 7-10. The complexes were allowed to settle for 15-20 minutes, filtered and then dried in air or in oven at 105-110°

Analytical data:

Found: Ni, 11.08; C, 45.26; H, 4.14; S, 12.06 and N, 21.12 percent.

For [Ni(*p*abts)$_2$], Calculated: Ni, 11.10; C, 45.39; H, 4.16; S, 12.10 and N, 21.18 percent.

Found: Cu, 10.00; C, 37.93; H, 3.78; S, 15.15 and N, 17.70 percent.

For [Cu(*p*abts)$_2$], Calculated: Cu, 10.06; C, 38.00; H, 3.80; S, 15.20 and N, 17.73 percent.

Results and Discussion

[M(*p*abts)$_2$$SO_4$ type of complexes of Ni(II) and Cu(II) were yellow in colour. These were found to be soluble in acetone and carbon tetrachloride. The complexes were stable upto 140°. *Bis*-chelate complex of the type [Cu(*p*abts)$_2$] of Cu(II) appeared green

while similar *bis*-chelate of Ni(II) was found yellowish green. These were also soluble in methanol, acetone and carbon disulphide.

Magnetic moment : Magnetic moment, $\mu_{eff}=0$ for both of the nickel(II)complexes showed them to be diamagnetic and square planar, involving dsp^2 hybridisations. μ_{eff} = 1.91 BM for [Cu(*p*abts)$_2$] SO_4 and μ_{eff} = 1.90 BM for [Cu(*p*abts)$_2$] suggested them to be paramagnetic. The contribution to paramagnetism in each complex was more than one unpaired electron spin equivalent but less than two. The discrepancy may be explained due to orbital contribution and distortion of octahedral structures to square planar ones, leading to dsp^2 hybridisation. No exact information regarding geometry of the Cu(II) complexes can be obtained.

TABLE 1—U.V. SPECTRA

Complexes	λ max (mμ)
[Ni(*p*abts)$_2$]SO_4	570,510,410,330
Ni(*p*abts)$_2$	520,440,320,260
[Cu(*p*abts)$_2$]SO_4	660,565,480,260
Cu(*p*abts)$_2$	650,505,380 –

[M(pabts)$_2$]SO_4 complexes:

The Ni(II) complex was found to be spin paired type. Excitation[8] of one electron from $1A_{1g}$ ground term leads to $1B_{1g}$ term. The bands at 440 mμ and 410 mμ in the spectrum of Ni(II)-complex have been assigned due to ($1A_{1g}\rightarrow 1B_{1g}$) transition. The band at 330 mμ has been assigned to the charge transfer band. The band due to 570 mμ accounts for the yellow colour of the Ni(II) complex. The band at 510 mμ may be probably due to slight contribution to ($1A_{1g}\rightarrow 3B_{1g}$) transition. These suggested the planar geometry of the Ni(II)-complex.

In the spectrum of the Cu(II) complex, the bands at 660 mμ was assigned to ($2B_{1g}\rightarrow 2A_{1g}$) transition. Moreover, the band at 565 mμ was attributed to ($2B_{1g}\rightarrow 2B_g$) transition. The band positions suggested the co-planar nature of the Cu(II)-complex. Out of the weak bands at 480 and 260 mμ, the latter has been accounted due to the charge transfer.

M(pabts)$_2$ complexes : The bands at 440 and 520 mμ in the spectrum of the Ni(II)-chelates were assigned due to ($1A_{1g}\rightarrow 1B_{1g}$) and ($1A_{1g}\rightarrow 3B_{1g}$) transitions. Moreover, the bands due to charge transfer were observed at 320 and 260 mμ in the spectrum of the Ni(II)-chelate. On the spin pair assumption of d^8 electrons in Ni led to $b_{2g}^2 . e_g^4 . a_{1g}^2$ (S=O) which suggested the square planar structure of the complex.

TABLE 2—I.R. SPECTRA

*p*abts cm^{-1}	[Ni(*p*abts)$_2$]SO_4 cm^{-1}	Ni(*p*abts)$_2$ cm^{-1}	Cu(*p*abts)$_2$$SO_4$ cm^{-1}	Cu(*p*abts)$_2$ cm^{-1}	
3465 bs	3460 bw	3450 bw	3410 bw	3415 bw	ν(NH)
3380	3380	3370	3390	3385	Co–NH–
3090 w	3085 w	–	3080 w	–	–
2875 2	2870 w	2870 w	2880 w	2880 w	=CH–str.
1670 ms	1660 w	1655 w	1665 w	1660 w	ν(C=O),NH or NH_2 bend
1645 s	1635 ws	1630 s	1640 vs	1635 vs	Sym C=N str.
1630 s	1620 w	1620 ws	1625 ws	1625 vs	Asym C=N or NH
1525 w	1510 w	1530 w	1535 ws	1535 s	δ(NH_2)+ν(CN)
1380 ms	1380 ws	1380 w	1390 ms	1385 ms	CH_3–CO, Sym-CH_3
1350 s	1320 ms	–	1330 s	–	ν(C=s), N–C–N ν(C–N) or C–NH_2
–	1100-30vs	–	1100-35vs	–	SO_4-2
–	–	1025 w	–	1000 bw	Ring Substitution
–	–	910 bw	–	905 bw	N–C=N or ν(C–SH)
860 b	8606 –	860 w	860 w	860 w	Paradisubstituted ring
–	–	765 w	–	775 w	ν(C–S)
–	530 s	520 s	480 bs	490 bs	ν(M–N)
–	525 ws	450 ws	435 ws	430bs	ν(M–S)
–	570 ws	–	455 ws	–	ν(M–N)+ν(M–S)

In the spectrum of the Cu(II)-chelate, the bands at 650 and 505 mμ were assigned to ($2B_{1g} \rightarrow 2A_{1g}$) and ($2B_{1g} \rightarrow 2E_g$) transitions respectively. These bands were found to be slightly polarised. The band at 380 mμ was very weak. The positions of the bands suggested the square planar geometry of the Cu(II)-chelate. The band at 505 mμ also explained the green colour of the complex.

Infrared Spectra :

I. R. spectra of the ligand and complexes were studied between 4000-200 cm^{-1} using KBr matrices and the results were placed in Table 2.

[M(pabts)$_2$]SO$_4$ complexes :

The band due to ν(C=S) at 1350 cm^{-1} in the spectrum of the ligand has been shifted downwards at 1320 and 1330 cm^{-1} in the spectra of the Ni(II) and Cu(II) complexes. This observation is supported by the earlier measurement by Pandey[3], who found ν(C=S) at 1300-20 cm^{-1} in the Cr(II)-complexes of the substituted benzaldehyde thiosemicarbazone. The decrease in frequency, without making any considerable modification of intensity suggested the coordination to Ni(II) or Cu(II) through sulphur atom of the C=S group.

The band at 1645 cm^{-1} in the spectrum of the ligand due to –CH=N and NH of hydrazine residue of the ligand decreased to 1635 and 1640 cm^{-1} in the spectra of the Ni(II) and Cu(II)-complexes. This further suggested the coordination to Ni(II) or Cu(II) through nitrogen atom of -CH=N- i.e., Schiff's base residue of the ligand. On complexation, a slight increase in intensity for Cu(II)-complex has been noted.

The coordination to metal atom through N of C=N of the Schiff's base residue has been supported by Pandey[3] and Pradhan[4].

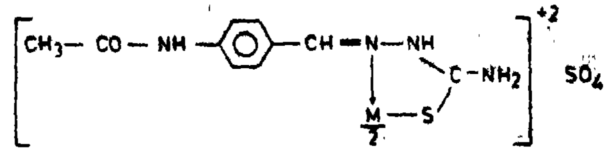
The sharp band at 1630 cm^{-1} was assigned to asymmetrical C=N frequency, which shifted to the lower frequencies i.e., at 1620 and 1625 cm^{-1} in the Ni(II) and Cu(II)-complexes. The decrease in intensity in case of Ni(II)-complex was attributed to the complex formation. Sahni and others[5] found sym (C=N) and asym (C=N) frequencies in the dibenzylidene dipicolonic acid complexes at 1640 and 1630 cm^{-1}.

ν(CN)+δ(NH_2) -Vibration frequency has been observed at 1525 cm^{-1} in the spectrum of the ligand. But that shifted upwards at 1530 and 1535 cm^{-1} in the Ni(II) and Cu(II) complexes. Increase in frequency on complex formation has also been reported by the earlier workers[4-6].

Broad sharp bands at 1100-30 and 1100-35 in the spectra of the Ni(II) and Cu(II)-complexes indicated clearly that the sulphate groups are ionic and existed in the complexes, out side the coordination spheres.

Some new bands which appeared at low frequencies in the spectra of the complexes were probably due to metal-nitrogen and metal-sulphur bond vibration frequencies. The sharp bands at 530 and 460 were assigned to ν(Ni–N) and ν(Cu–N) frequencies. The bands at 525 and 435 may be attributed to ν(Ni–S) and ν(Cu–S) frequencies respectively.

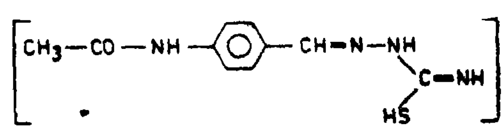
On the basis of the above evidences, it is obvious that the ligand '*pabts*' is bidentate in nature and the complexes can be represented by the following structure.



Where M=Ni (II) and Cu (II)

M(pabts)$_2$ complexes :

In an alkaline medium, i.e., at increased *p*H values H atom of NH_2 of the ligand contributes much to S than to N atom. Thus a tautomeric effect causes the ligand to undergo the thioenolic form, in which the double bond character of (C=S) decreases to (C–S) one, which is only possible after formation of C–SH group i.e., thioenolic group. In this case, replacement of proton(H^+) form the acidic SH group and donation through N atom of Schiff's base residue become the potential affairs. The deprotonation at high *p*H values has been claimed in several cases. The bands at 1025 and 1000 cm^{-1} in the spectra of Ni(II) and Cu(II) respectively may be probably due to ν(C–SH) frequencies. Srivastva and others[7] suggested ν(C–S) at (1010+10) and 990 cm^{-1} in triprophyltin dithiocarbamate. Moreover, the replacement of H of SH group of the thioenolic ligand has been confirmed by the presence of clear bands due to ν(C–S) at 765 and 775 cm^{-1} in the spectra of Ni(II) and Cu(II) complexes. Murthy and others[8] suggested ν(C–S) at 720 and 727 cm^{-1} for Cu(II) and Ni(II) complexes.



(Thioenolic form)

Mohapatra and others[9] suggested ν(C=S) at 1235 cm^{-1} Ghosh and others[10] suggested ν(C=S) in thiocyanate complexes of Pt group metals at 690–756 cm^{-1}. Thus ν(C=S) or ν(C–S) frequency varies largely from one to another complexes.

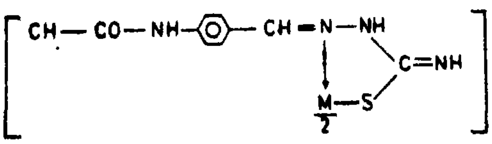
ν(C=N) which was found in the spectrum of the ligand at 1645 cm^{-1}, decreased and modified intensity at 1630 and 1635 cm^{-1} in the spectra of Ni(II) and Cu(II)-complexes. This clearly showed the coordination through nitrogen atom of CH=N (Schiff's base residue).

Low frequency bands at 520 and 490 cm^{-1} were assigned to ν(M–N), which is supported by the author's earlier work[11] for identical ligand site. The

bands at 450 and 430 cm^{-1} may be probably due to ν(M – S) in the Ni(II) and Cu (II)-complexes respectively.

Mohapatra[9] assigned ν(Co – S), at 260 cm^{-1}. Srivastva[7] found ν(Sn – S) at 370 cm^{-1}. Udupa[12] showed Mo – S at 470 cm^{-1} in the thiosalts. The very low frequency of ν(M – S) may be probably due to increased dimension of sulphur atom.

Thus the structures of the chelate complexes of Ni(II) and Cu(II) can be represented as follows :—



Where M=Ni (II) and Cu (II) .

Acknowledgement

The author is thankful to Dr. Satya P. Popli, Medicinal Deptt., C.D.I.R., Lucknow, who helped in recording the various spectral data and also to Dr. L. K. Mishra, Patna Science College, who provided instrument for magnetic study. The author is sincerely thankful to Dr. Y. Thakur, Head of Chemistry Dept., Mithila University, Darbhanga who helped in study of various analyses and gave valuable suggestions.

References

1. J. A. CRIM and H. G. PETERING, *Cancer Res.*, 1967, **27**, 1278.
2. B. N. FIGGIS, Introduction to Ligand Fields, Wiley Eastern Ltd., New Delhi, 1976, 314.
3. U. N. PANDEY, *J. Indian Chem. Soc.*, 1978, **55**, 654.
4. B. PRADHAN and D. V. RAMANA RAO, *J. Indian Chem. Soc.*, 1977, **54**, 136.
5. S. K. SAHNI, S. P. GUPTA, S.K. SANGAL and V.B. RANA, *J. Indian Chem. Soc.*, 1977, **54**, 200.
6. B. BEECROFT. M. J. M. CAMPBELL and R. GROZES KOBIAK, *J. Inorg. Nuclear Chem.*, 1974, **36**, 55.
7. T. N. SRIVASTVA and ROSHMI BALA RASTOGI, *J. Indian Chem. Soc.*, 1978, **55**, 521.
8. U. K. MURTHY, N. D. J. JAGNIK and M. G. PRANJPE, *J. Indian Chem. Soc.*, 1976, **53**, 419.
9. B. B. MOHAPATRA, B. K. MOHAPATRA and S. GURU, *J. Indian Chem. Soc.*, 1978, **55**, 513.
10. S. P. GHOSH, P. BHATTACHARJEE, L. DUBEY and L. K. MISHRA, *J. Indian Chem. Soc.*, 1977, **54**, 230.
11. C. B. MAHTO, *Acta, Ciencia Indica*, 1978, **4**, 245.
12. M. R. UDUPA, *J. Indian Chem. Soc.*, 1976, **53**, 340.

J. Indian Chem. Soc.,
Vol. LVII, May 1980, pp. 485-489

Study of the Complex Compounds of Some Transition Metals with Isonicotinic Acid Hydrazide

C. B. MAHTO

Department of Chemistry, Gopalganj College, Gopalganj

Manuscript received 27 November 1979, accepted 30 December 1979

The complex compounds of isonicotinic acid hydrazide, (L) (abbreviated "INAH") with Ni(II), Cu(II), Fe(II), Co(II) and Pd(II) of the molecular formulae, $ML_2.SO_4.2H_2O$, (where M = Ni, Cu, Fe and Co) and $M'L_2Cl_2$ (M' = Pd) have been prepared and characterised. The structures of the complexes have been established on the basis of their elemental analysis, ir, uv and magnetic studies. The Ni(II), Cu(II), Fe(II) and Co(II)-complexes were found to be octahedral and paramagnetic, while Pd(II)-complex was concluded to be square planar and diamagnetic.

THE ligand isonicotinic acid hydrazide (INAH), which is an important antitubercular drug and has potential sites for the metal ions, has been used in the complex formation, with a view that the complexes isolated, may be of the biological importance. Certain other hydrazides of varying coordination sites for the metal ions, have been studied by the earlier workers. The present paper reports five complex compounds of INAH with nickel(II), copper (II), iron (II), cobalt(II) and palladium(II).

Materials and Ligands :

$NiSO_4 . 6H_2O$, $CuSO_4 . 5H_2O$, $FeSO_4 . 7H_2O$ and $CoSO_4.7H_2O$ all of E. M. analytical reagent grade and $PdCl_2$(A.M.) grade were employed.

0.002(*M*) ethanolic solution of INAH was used.

Complexes :

Ni(II), Cu(II), Fe(II) and Co(II) complexes :

0.001(*M*) aqueous ethanolic solution of each of Ni(II), Cu(II), Fe(II) and Co(II) was treated with 0.002(*M*) ethanolic solution of the ligand, i.e., in 1 : 2 molar ratio and then heated on the water-bath for $1-1\frac{1}{2}$ hours. The microcrystalline complexes, with characteristic colours were formed. The complexes were filtered, washed 3-4 times with alcohol and then dried over fused $CaCl_2$ in a dessicator.

Pd(II)-complex :

0.001(*M*) Pd(II)-solution in ethanol was treated with 0.002 (*M*) ethanolic solution of the ligand. The complex was isolated by treating the contents over water bath for an hour. The complex was filtered, washed with ethanol and dried over fused $CaCl_2$ as usual.

Results and Discussion

The *p*H values, at which the complexes were formed, colours of the complexes, results on the elemental analyses and magnetic moment values have been placed in Table 1.

TABLE 1

Complexes	*p*H of formation	Colours	% M found (calcd.)	% C found (calcd.)	% H found (calcd.)	% N found (calcd.)	μ_{eff}, BM (25°c)
$Ni(INAH)_2SO_4.2H_2O$	3.5	Blue yellow	12.62 (12.63)	30.95 (30.98)	3.83 (3.87)	18.02 (18.07)	3.09
$Cu(INAH)_2.SO_4.2H_2O$	4.0	Greenish blue	13.30 (13.31)	30.60 (30.67)	3.70 (3.83)	17.82 (17.88)	2.51
$Fe(INAH)_2.SO_4.2H_2O$	4.0	Yellowish brown	12.00 (12.09)	31.10 (31.17)	3.85 (3.89)	18.06 (18.18)	5.82
$Co(INAH)_2.SO_4.2H_2O$	3.5	Pink	12.65 (12.67)	30.90 (30.97)	3.81 (3.87)	18.00 (18.06)	4.78
$Pd(INAH)_2.Cl_2$	3.0	Yellow	23.56 (23.67)	31.85 (31.90)	3.06 (3.10)	18.40 (18.60)	0.00

These complexes were soluble in water, methanol and carbon tetrachloride. The complexes were found quite stable upto 130°-40°.

Magnetic moment :

Magnetic moment, μ_{eff}, for Ni(II)-complex was found to be 3.09 BM, which suggested it to be paramagnetic with octahedral structure μ_{eff} for Cu(II)-complex was determined to be 2.51 BM, which was pretty large from paramagnetism contribution due to one unpaired electron spin, although a bit less than 2.82 BM, a value corresponding of two unpaired electrons spin equivalent. The discrepancy may be explained because of a bit shift of octahedral symmetry towards the distorted octahedral one μ_{eff}=5.82 BM, in case of Fe(II)-complex suggested it to be paramagnetic and octahedral[1]. In case of Co(II)-complex, μ_{eff}= 2.78 BM, might be attributed due to high symmetry component[2] in octahedral geometry and also free from partial covalent character. μ_{eff} = 0 in case of Pd(II)-complex, showed it to be diamagnetic having square planar geometry, involving dsp^2 hybridisation.

U. V.-vis spectra :

U. V. -vis spectra of the complexes were studied in methanol and data were placed in Table 2.

of the band suggested the octahedral geometry of the Ni(II)-complex.

Broad band at 13422 cm^{-1} might be regarded due to 2 $E_g \rightarrow 2T_{2g}$ transition. It was found asymmetric on account of splitting by a low symmetry ligand field component. Absence of a band around 18181 cm^{-1} discarded the possibility of square planar geometry. However, a band at 15151 cm^{-1} suggested the distortion of octahedral geometry of the complex. The band at 23256 cm^{-1} has been attributed due to charge transfer. All these band positions suggested the distorted octahedral geometry for Cu(II) complex.

The spectra of Fe(II)-complex showed the charge transfer band at 19387 cm^{-1}. The band at 25125 cm^{-1} was probably due to $1A_{1g} \rightarrow 1T_{1g}$ transition, which also might be regarded a charge transfer band. A broad band at 12193 cm^{-1} due to 5 $T_{2g} \rightarrow 5\ E_g$ transition suggested the octahedral geometry of Fe(II)-complex. In this case, Dq value and second and first frequencies ratio were found to be 121 cm^{-1} and 1.51 respectively.

A very weak band of low intensity at 10746 cm^{-1} in the spectrum of Co(II)-complex has been assigned to

TABLE 2

Complexes	λ max, nm	Frequency (V) cm^{-1}	Transitions	Dq, cm^{-1}	B cm^{-1}	$\frac{v_2}{v_1}$	β
$Ni(INAH)_2SO_4.2H_2O$	402	24875 (V_3)	$3A_{2g} \rightarrow 3T_{1g}$ (P)				
	520	15300 (V_2)	$3A_{2g} \rightarrow 3T_{1g}$ (F)				
	920	10967 (v_1)	$3A_{2g} \rightarrow 3T_{2g}$ (F)	109	956	1.84	0.92
$Cu(INAH)_2SO_4.2H_2O$	430	23256 (v_4)	C → T				
	660	15151 (v_3)	$2B_1 \rightarrow 2E_g$				
	745	13422 (v_2)	$2E_g \rightarrow 2T_{2g}$				
	862	11600 (v_1)	$2B_1$ $2A_{1g}$	116	...	1.16	...
$Fe(INAH)_2SO_4.2H_2O$	398	25125 (v_3)	$1A_{1g} \rightarrow 1T_{1g}$				
	515	19387 (V_2)	C → T				
	820	12193 (v_1)	$5T_{2g} \rightarrow 5E_g$	121	...	1.51	...
$Co(INAH)_2SO_4.2H_2O$	460	21738 (v_3)	$4T_{1g}(F) \rightarrow 4T_{1g}(P)$	107	975	1.85	0.87
	502	19920 (v_2)	$4T_{1g}(F) \rightarrow 4A_{2g}(F)$				
	930	10746 (v_1)	$4T_{1g}(F) \rightarrow 4T_{2g}(F)$				
$Pd(INAH)_2Cl_2$	280	35714 (v_3)	C→T				
	320	31238 (v_2)	$1A_{1g} \rightarrow 1E_g$				
	420	24389 (v_1)	$1A_{1g} \rightarrow 1B_{1g}$	243		1.29	

The bands at 24875, 15300 and 10967 cm^{-1} have been assigned to 3 $A_{2g} \rightarrow 3T_{1g}$ (P), $3A_{2g} \rightarrow 3T_{1g}$(F) and 3 $A_{2g} \rightarrow 3T_{2g}$ (F) respectively. Transition at 10967 cm^{-1} might be attributed to spin allowed transition, while that at 19230 cm^{-1} has been explained to be spin forbidden transition. Dq was found to be 109 cm^{-1} on the basis of first frequency and ratio of v_2 and v_1 was 1.84. The spin allowed transition might be regarded due to transition arising in the complex when passing from O_h to D_{4h} symmetry. The positions

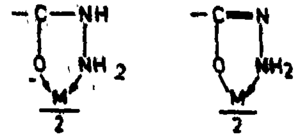
4 T_{1g} (F)→4 T_{2g} (F) transition, which explained the pink colour of the complex also. The bands at 21738 and 19920 cm^{-1} were assigned due to $4T_{1g}$ (F)→ 4 A_{2g}(F) and $4T_{1g}$ (F) →$4T_{1g}$ (P) transitions, respectively. The possibility of effect of low symmetry ligand field component on a single term might not be made a base to explain them. The first frequency showed Dq to be 107cm^{-1} and v_2 and v_1 ratio was found to be 1.85. The positions of the bands suggested confidently the octahedral geometry of Co(II)-complex.

A band at 24389 cm^{-1} in the u.v. spectra of Pd(II)-complex has been assigned to $1A_{1g} \rightarrow 1B_{1g}$ ($a_{1g}^{2} \rightarrow a_{1g}^{1}$, b_{g}^{1}) transition. It suggested the square planar geometry of Pd(II)-complex. The band at 31238 cm^{-1} which was shoulder on the charge transfer band at 35714 cm^{-1} was a ligand field origin probably due to $1A_{1g} \rightarrow 1B_{g}$ transition.

I. R. spectra :

The I. R. spectra of the ligand and complexes were studied in KBr phase between 4000-200 cm^{-1}, and the results are placed in Table 3.

Moreover, M–O band could be formed only when oxygen atom of C=O group[4] donated a lone pair of electrons to the metal ions or by the replacement of hydrogen atom of OH group of the enolic from[6] (amidol system) of the ligand.



I II

TABLE 3

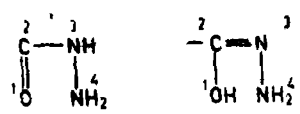
INAH, cm^{-1}	Ni(II), cm^{-1}	Cu(II), cm^{-1}	Fe(II), cm^{-1}	Co(II), cm^{-1}	Pd(II), cm^{-1}	Assignments
—	3580 bs	3550 s	3530 s	3560 s		OH str. of H_2O
3430 vs	3370 s	3380 vs	3385 s	3375 s	3370 s	$\nu(NH_2)$
3310 s	3150 s	3155 ms	3145 ms	3160 ms	3150 ms	ν sym (NH)
3210 s	3060 ms	3080 vs	3075 ms	3055 ms	3065 ms	ν_s sym (NH_2)
1715 s	1675 s	1670 s	1680 s	1665 ms	1675 s	ν(C=O)
1640 s	1620 w	1630 w	1630 w	1635 w	1625 w	NH_2 deform or bend +OCN
1605 s	1590 s	1560 s	1565 s	1580 s	1595 s	Hetrocyclic ring+ring asym (C=N)
1490 ms	1500 w	1495 w	1505 ms	1510 ms	1500 ms	ν(C–N)
1250 ms	1390 ms	1390 ms	1380 ms	1395 ms	1385 ms	(NH) νsym (C=N)
	1200 w	1195 ms	1205 ws	1210 ms	1205 w	(NH)
	1130 vs	1130 vs	1125 vs	1135 vs		SO_4^{-2}
	1105 s	1100 s	1110 s	1105 s	1110 s	(C–O)
995 w	995 w	990 w	985 w	990 w	995 w	N–N made
950 w	950 w	945 w	945 w	950 w		C–H out of plane deform or SO_4^{-2}
890 s	890 ms	890 ms	885 ms	890 ms	885 ms	ring with 2 H adjacent +NH out of plane bend.
	785 s	790 s	780 ms	785 s		coordinated H_2O
745 s	745 s	745 s	740 s	750 s	745 s	Mono substituted ring.
685 ms	685 ms	685 ms	680 ms	685 ms	680 ms	(C=O) out of plane
	630 s	640 ms	635 ms	635 ms		Coordinated H_2O
580 w	575 w	570 w	565 w	565 w	570 w	NH_2 rocking.
	530 bw	520 w	530 ms	540 ms	510 ms	(M–O)
	520 w	510 bs	500 w	505 w	508 ms	ν(M–N)
	500 ms	490 s				ν(M–O)+ν(M–N)
460 w	465 w	470 w	465 w	470 w	465 w	ν(C=O) in plane.

The band at 3430 cm^{-1} due to $\nu(NH_2)$, in the spectrum of the ligands[2] was found to decrease at 3370, 3380, 3385, 3375 and 3370 cm^{-1} in the spectra of the Ni(II), Cu(II), Fe(II), Co(II) and Pd(II) complexes respectively, showing that the coordination has taken place through nitrogen atom of NH_2 group of the hydrazine residue.

The bands at 3580, 3550, 3530 and 3560 cm^{-1} in the Ni(II), Cu(II), Fe(II) and Co(II)-complexes have been assigned to OH stretching frequencies of the coordinated water molecules.

Further, the appearance of the bands of medium intensites around 630-640 cm^{-1} and the sharp bands around 780–790 cm^{-1} in the spectra of Ni(II), Cu(II), Fe(II) and Co(II)-complexes suggested that two water molecules[4] were coordinated to the respective metal ions.

At a glance, the latter probability appeared more evident due to the steric hindrance of the aromatic heterocyclic ring, linked with the carbonyl carbon atom, adjacent to which was NH group of the hydrazine residue. Due to that, H atom of NH group would contribute more to greater electronegative oxygen atom of C=O group, rather than to immino nitrogen atom.



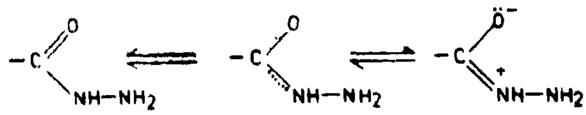
(Keto form) (Enol form)

III IV

Which one of the forms III and IV (both having requisite sites) responsible for the complex formation

might be concluded on the basis of presence of ν(C – N) which was observed at 1490 cm^{-1} in the spectrum of the ligand shifted to 1500, 1495, 1505, 1510 and 1500 cm^{-1} in the Ni(II), Cu(II), Fe(II), Co(II) and Pd(II)-complexes respectively. Thus *form* III seemed more prominent for the coordination than the form IV, which might be prominent at high *p*H values, where replacement of H atom or deprotonation appeared easier.

ν(C = O) frequency which was observed in 1715 cm^{-1} in the spectrum of the ligand, shifted downwards[1] at 1675, 1670, 1680, 1665 and 1675 cm^{-1} in the Ni(II), Cu(II), Fe(II), Co(II) and Pd(II)-complexes respectively. This suggested that the coordination had taken place through oxygen atom of C = O group. After coordination intensities remained unchanged. Due to the co-ordination, a loss of lone pair of electrons of oxygen atom was further compensated by the electrons of C = O bond, which resulted into a decrease of double bond character of C – O group and consequently increase of C – N double bond character[1,7].



(V) (VI) (VII)

The band at 1250 cm^{-1} in the spectrum of the ligand splitted into two components, i.e., in the ranges, (1195 – 1210) and (1380 – 1395) cm^{-1} in the spectra of the complexes. The latter components might be due to νsym(C = N), developed in the spectra of the complex due to increase of (C – N) double bond character. Sharp bands between (1605 – 1560) cm^{-1} in the spectra of the ligand and the complexes were assigned to the aromatic ring including (C = N) asymetric frequency of the ring. The bands around (1110 – 1100) cm^{-1} in the spectra of the complexes, which were assigned to ν(C – O) frequencies[8], appeared after coordination of carbonyl oxygen atom to metal ions and decrease of double bond character of C=O. The appearance of ν(C – O) frequencies in the complexes, might not be explained in terms of the replacement of H atom of the enolic ligand, because the complexes have been formed at low *p*H values where deprotonation appeared difficult[8].

Further the very sharp bands around (1135 – 1125) cm^{-1} in the spectra of the complexes [except Pd(II)], have been assigned to the ionic nature of sulphate group[8,9] with T_d-symmetry in the complexes.

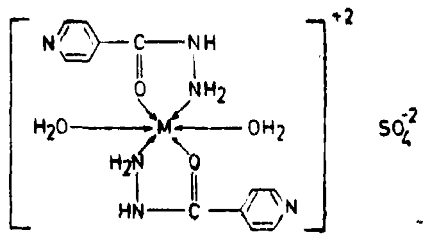
The sharp band at 640 cm^{-1} in the spectrum of the ligand was assigned due to NH_2 deformation, associated with OCN band shifted downwards around (1635 – 1620) cm^{-1} in the complexes and diminished the frequencies. The bands around (995 – 985), (950 – 945) and (890 – 885) cm^{-1} in the spectra of the ligand and complexes have been assigned to N-N mode of vibration[1], C-H out of plane deformation and heterocyclic ring having two adjacent hydrogen atoms[9], probably coupled with the band due to NH out of plane deformation respectively.

The ir spectra of Ni(II)-complex showed broad diffused nature of bands in the region 3600 – 3200 cm^{-1} probably due to overlap of NH, NH_2 and OH mode of coordinated water molecules[8].

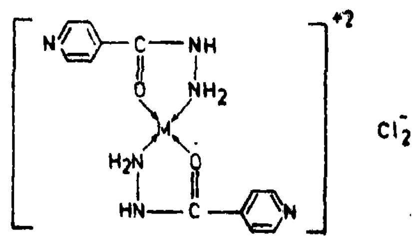
The low frequency bands at 530, 520, 530, 540 and 510 cm^{-1} in the spectra of the complexes only, were assigned to ν(Ni-O), ν(Cu-O), ν(Fe-O), ν(Co-O) and ν(Pd-O) respectively[3,4]. Sahni and others[1] observed ν(M-O) at still lower frequencies in the complexes of pentadentate ligand having identical system and trivalent metals.

The bands at 520, 510, 500, 505 and 508 cm^{-1} in the spectra of the complexes have been assigned to ν(Ni-N), ν(Cu-N), ν(Fe-N), ν(Co-N) and ν(Pd-N) respectively[1,4]. The spectrum of Pd(II)-complex did not show the bands for the coordinated water molecules.

On the basis of the above evidences, it has been concluded that the ligand is neutral and bidentate in nature and the tentative structures of the electrolytic cationic complexes can be represented as follows :—



(VIII)
Where, M = Ni, Cu, Fe and Co.



(IX)
Where, M^1 = Pd.

Acknowledgement

The author is thankful to Dr. Satya P. Popli, Scientist in charge, Medicinal Department, C. D. I. R., Lucknow who helped in the study of the ir and uv

spectroscopy of the complexes. The author is also grateful to Dr. L. K. Mishra, Patna Science College, who provided instrument for the magnetic study. Lastly, the author is sincerly thankful to Dr. Y. Thakur, University Head of Chemistry, Mithila University, Darbhanga who provided facilities for the various analyses and gave the valuable suggestions.

References

1. S. K. Sahni, S. P. Gupta, S. K. Sangal and V.B. Rana, *J. Indian Chem. Soc.*, 1977, 54, 200.
2. P. Singh, V. Singh, R. Pal and R. L. Goel, *J. Indian Chem. Soc.*, 1978, 55, 33.
3. C. B. Mahto, *Acta Ciencia Indica*, 1978, 4, 3, 245.
4. N. S. Bhave and R. B. Kharat, *J. Indian Chem. Soc.*, 1979, 56, 244.
5. L. S. Sacconi, *J. Amer. Chem. Soc.*, 1952, 74, 4503; Ag. Offe, N.G. Steiken and Z. Momagh, *Z. Naturforsch*, 1952, 7B, 426.
6. H. H. Fox, J. T. Gibbas and A. Motchane, *J. Org. Chem.*, 1956, 21, 349.
7. J. Das, *J. Indian Chem. Soc.*, 1977, 54, 278.
8. N. Saha and D. Bhattacharyya, *J. Indian Chem. Soc.*, 1977, 54, 143.
9. Subhas-Satish and V. P. Kudesia, Spectrum Analysis, Pragati Prakashan, Meerut, 1972, p. 233.

J. Indian Chem. Soc.,
Vol. LVII, May 1980, pp. 490-492

Derivatographic Studies of Acid Maleato Complexes of Some Divalent Metals

H. C. MISHRA and M. P. NAIK

Chemistry Department, Ranchi University, Ranchi-8

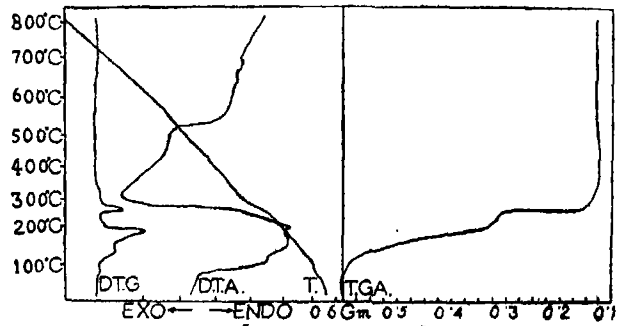
Manuscript received 18 September 1979, accepted 30 December 1979

Acid maleato complexes of maleic acid (Mal. H), with Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) of the formula [M(Mal. H)$_2$ (H$_2$O)$_4$] [M=Co(II), Ni(II), Cu(II), Zn(II)] and [M$_1$ (Mal. H)$_2$(H$_2$O)$_2$] [M$_1$ = Cd(II)] have been studied derivatographically. A number of intermediate products were obtained which do not correspond to any simple compound but are intermediate between those of normal and acido complexes. A comparison of the different transition temperatures of the various acido complexes do not show any correlation between the thermal properties of the complex and the physical or chemical properties of metal ions.

EDGE[1] has studied the thermal decomposition of vanadyl oxyanion maleic acid complex. Mc Ginn *et al*[2] have also reported the thermal decomposition of normal nickel maleate [Ni(Mal)$_2$(H$_2$O)$_2$]. However, none have reported derivatographic studies of acid maleato complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II).

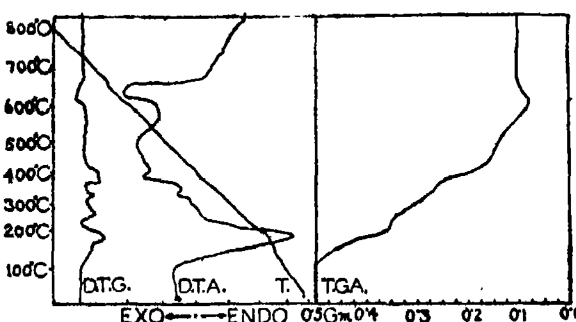
Experiment and Results

Acid maleato complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) have been prepared by our own method[3]. The derivatography of the system of Paulik Paulik and Erdey manufactured by M/s M.O.M. (Hungarian Optical Works) has been employed for the



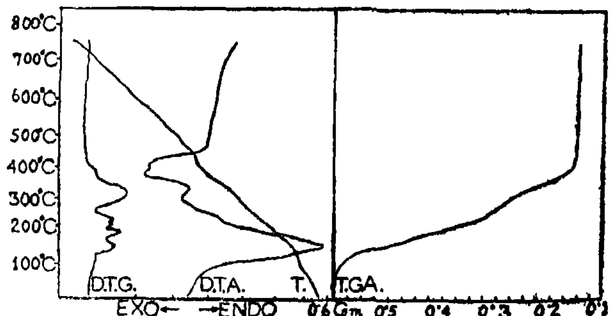
[Cu(Mal.H)$_2$(H$_2$O)$_4$]

Fig. 3



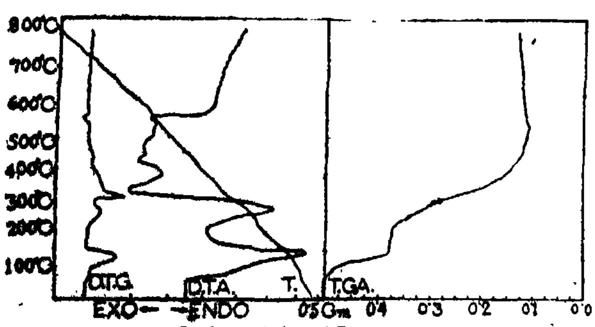
[Co(Mal.H)$_2$(H$_2$O)$_4$]

Fig. 1



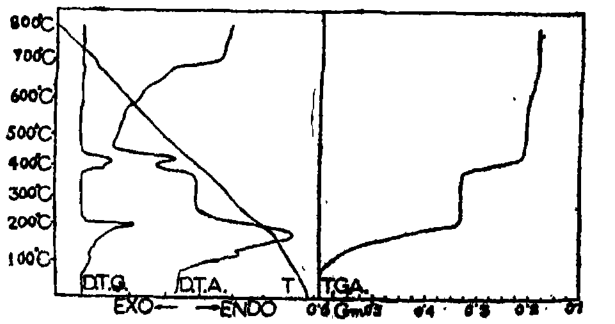
[Zn(Mal.H)$_2$(H$_2$O)$_4$]

Fig. 4



[Ni (Mal.H)$_2$(H$_2$O)$_4$]

Fig. 2



[Cd(Mal.H)$_2$(H$_2$O)$_2$]

Fig. 5

present study. The instrument records the different functions (Temperature T, D.T.G., D.T.A. and T.G.A.) photographically. The instrument rules chart according to programme of time and temperature. For differential thermal analysis ignited alumina has been used as the inert meterial and ceramic sample holders have been used for both the test and inert substances. The material has been used loose without being packed. Thermocouple does not come in contact with meterial in the holders. 500 to 600 mg of finely powdered material have been employed for the test. The sample holder is kept in such a way that the tip of the thermocouple in both the holders are Pt-13 percent Rh/Pt. The height of the test material is maintained almost equal to that of inert material in the reference sample holder. About 500 to 600 mg of sample is taken in ceramic crucible and heating rate of 8°/min upto 800° is maintained in static air. Results have been presented in Table 1 and combined curves of T, D.T.G., D.T.A. and T.G.A. are presented in Figs. 1-5.

During heat treatment a volatile substance was collected over cold glass rod. It was identified to be maleic acid by chemical analysis and m.p. determination, 131°. After heat treatment the end product in each case has been confirmed by chemical analysis and thin layer chromatography. The chemicals used were either of B.D.H. or E. Merk (A.R. Grade).

Discussion

It can be seen in general that the acid maleato complexes are completely dehydrated along with or without partial loss of ligand in first step. The composition of intermediates of first step (except Co and Zn where simply they are dehydrated) second step and third step (except Cu and Cd) do not correspond to any simple compound but are intermediate between these of normal and acido complexes. On the basis of derivatographic analysis, the acid maleato complexes may be grouped in the following two classes—

1. In this class, after dehydration and partial loss of ligand, metallic carbonate is formed which at higher temperature decomposes (a) to metallic oxide as in case of Zn-complex and (b) to free metal which

TABLE—1

	Transition	Temp. range	Curve
$[Co(Mal.H)_2(H_2O)_4]$	→ $Co(Mal.H)_2$	100–170	Endothermic
$Co(Mal.H)_2$	→ $Co(Mal.H)_{1.70}$	170–220	,,
$Co(Mal.H)_{1.70}$	→ $Co(Mal.H)$	250–325	Exothermic
$Co(Mal.H)$	→ $CoCO_3$	350–400	,,
$CoCO_3$	→ Co	400–560	,,
Co	→ CoO	560–650	,,
$[Ni(Mal.H)_2(H_2O)_4]$	→ $Ni(Mal.H)_{1.85}$	70–120	Endothermic
$Ni(Mal.H)_{1.85}$	→ $Ni(Mal.H)_{1.32}$	210–300	,,
$Ni(Mal.H)_{1.32}$	→ $Ni(Mal.H)_{0.50}$	300–390	Exothermic
$Ni(Mal.H)_{0.50}$	→ NiO	390–470	,,
$[Cu(Mal.H)_2(H_2O)_4]$	→ $Cu(Mal.H)_{1.20}$	80–190	Endothermic
$Cu(Mal.H)_{1.20}$	→ $Cu(Mal.H)_{0.80}$	190–250	,,
$Cu(Mal.H)_{0.80}$	→ CuO	250–350	Exothermic
$[Zn(Mal.H)_2(H_2O)_4]$	→ $Zn(Mal.H)_2$	75–140	Endothermic
$Zn(Mal.H)_2$	→ $Zn(Mal.H)_{1.13}$	140–250	,,
$Zn(Mal.H)_{1.13}$	→ $Zn(Mal.H)_{0.80}$	250–350	Exothermic
$Zn(Mal.H)_{0.80}$	→ $ZnCO_3$	350–390	,,
$ZnCO_3$	→ ZnO	390–450	,,
$[Cd(Mal.H)_2(H_2O)_2]$	→ $Cd(Mal.H)_{1.44}$	80–160	Endothermic
$Cd(Mal.A)_{1.44}$	→ $Cd(Mal.H)_{0.85}$	160–250	,,
$Cd(Mal.H)_{0.85}$	→ CdO	370–410	Exothermic
CdO	→ Cd	590–700	,,

is followed by oxide formation as in case of Co-complex.

2. In this class metallic carbonate is not formed as an intermediate product after dehydration and loss of ligand but decomposition of acid maleato complex leads to the formation of (a) only metallic oxide as in cases of Ni and Cu complexes and (b) metallic oxide followed by free metal as in case of Cd-complex.

A comparison of the decomposition temperatures of different acid maleato complexes do not reveal any general correlation between the thermal properties of the complexes and the physical or chemical properties of the metal ion. But the temperature at which the oxide is formed varies with the basicity of the metal Co>Ni~Zn>Cd>Cu.

The deposition of maleic acid over cold glass rod is due to the thermal dissociation of the acid maleato complex to the normal complex and maleic acid according to the reaction

$$2M(Mal.H)_x \rightarrow M_2\ Mal_x + X\ Mal.H_2$$

and this is favoured at higher temperature. Products intermediate between normal and acido complex seems to be the incomplete thermal disproportionation. We could not conclude as to why species intermediate between acido and normal complexes are formed.

Acknowledgement

We are thankful to Mr. Satyen, C.F.R.I., Dhanbad for his co-operation and one of the authors (M.P.N.) thanks the U.G.C., New Delhi for the award of a Junior Research Fellowship.

References

1. ROBERT A. EDGE, *J. Less—Common Metals*, 1969, **18**, 325.

2. M. J. MCGINN, B. R. WHEELER and A. K. GALWEY, *Trans. Faraday Soc.*, 1971, 67, 1480.

3. M. P. NAIK, Ranchi University, Ph.D. Thesis, 1978.

J. Indian Chem. Soc.,
Vol. LVII, May 1980, pp. 493-496

Refractometric Studies on the Interaction of Some Metal Acetylacetonates with Iodine

R. SAHAI* , V. SINGH and (Miss) REKHA VERMA

Department of Chemistry, V. S. S. D. College, Kanpur-208 002

Manuscript received 6 September 1979, accepted 30 December 1979

Formation of molecular complexes between metal acetylacetonates of Be(II), VO(II), Al(III), Cr(III), Fe(III) and Co(III) as donors and iodine as acceptor has been studied in carbon tetrachloride using refractometric and differential refractometric techniques. The equilibrium constants (K_1) and extent of electronic polarization (α) of these complexes have been determined. The refractometric titration technique has indicated 1:1 stoichiometry of these complexes. These data provide further support on the pseudo-aromatic character of metal acetylacetonate chelate rings.

SPECTROPHOTOMETRIC[1], conductometric[2] and dielectric studies[3] have indicated that like aromatics, co-ordinatively saturated, neutral monomeric metal acetylacetonates, $M(acac)_n$, form molecular complexes with iodine by donation of electron density from chelate rings. In order to provide further support on the pseudo-aromatic character of metal acetylacetonate chelate rings, the charge-transfer complex formation ability of Be(III), VO(II), Al(III), Cr(III), Fe(III) and Co(III) chelate rings with iodine has been studied employing refractometric and differential refractometric techniques.

Experimental

Metal acetylacetonates of Be(II)[4], VO(II)[5], Al(III)[6], Cr(III)[7], Fe(III)[8] and Co(III)[9] were prepared and purified as reported in the literature. The acetylacetone (BDH) was redistilled before use. Iodine (A.R.) was resublimed. Analytical grade carbon tetrachloride was redistilled before use.

Stock solutions of donors [$M(acac)_n$ where M= Be(II), VO(II), Al(III), Cr(III), Fe(III) and Co(III)] and acceptor (iodine) were prepared by weighing on an analytical balance and then diluted to the desired volume in volumetric flasks by carbon tetrachloride. The solution employed for measurements were prepared from stock solutions by pipetting the calculated volumes into 10 ml volumetric flasks and then diluted subsequently with the same solvent. All the stock solutions were prepared on the day of measurements. All the measurements were carried out at room temperature.

The refractive indices have been measured by Bousch & Lomb refractometer, with an accuracy of ±0.0002. The equilibrium constant (K_1) and extent of electronic polarization (α) of 1:1 molecular complexes have been calculated by using equations (1, 2 and 3) developed by Sahai *et al.*[10-12],

$$\frac{\delta\phi}{C_D^0}=\frac{K_1C_A^0}{\alpha(1+K_1C_A^0)}-\frac{K_1\delta\phi}{(1+K_1C_A^0)^2} \quad \dots (1)$$

$$\frac{\Delta\phi}{C_D^0}=\frac{K_1C_A^0}{\alpha(1+K_1C_A^0)}-\frac{K_1\Delta\phi}{(1+K_1C_A^0)^2} \quad \dots (2)$$

$$\frac{\Delta\Omega C_{DA}}{C_D^0}=\frac{K_1C_A^0}{\alpha(1+K_1C_A^0)}-\frac{K_1\Delta\Omega C_{DA}}{(1+K_1C_A^0)^2} \quad \dots (3)$$

where C_D^0 and C_A^0 are the initial concentrations of donor (D) and acceptor(A) respectively, and α is the extent of electronic polarization. $\delta\phi$, $\Delta\phi$ and $\Delta\Omega C_{DA}$ may be calculated by the following relations,

$$\delta\phi=10^3(\phi-\phi_0)=6000(n-n_0)n_0/(n_0^2+2)^2 \quad \dots (4)$$

$$\Delta\phi=10^3(\phi-\phi_A)=6000(n-n_A)n_A/(n_A^2+2)^2 \quad \dots (5)$$

$$\Delta\Omega C_{DA}=10^3(\phi-\phi_D)-10^3(\phi_A-\phi_0)$$
$$=\{6000(n-n_D)n_D/(n_D^2+2)^2\}$$
$$-\{6000(n_A-n_0)n_0/(n_0^2+2)^2\} \quad \dots (6)$$

where n, n_D, n_A, n_0 are the refractive indices of solution (donor+acceptor), donor, acceptor and solvent respectively. ϕ, ϕ_D, ϕ_A and ϕ_0 are the refraction per cm³ due to solution, donor, acceptor and solvent respectively, which may be calculated as reported earlier[10,11]. As expected from equations (1,2 and 3), the plots of $\delta\phi$ *vs* $\delta\phi/C_D^0$, $\Delta\phi$ *vs* $\Delta\phi/C_D^0$ and $\Delta\Omega C_{DA}$ *vs* $\Delta\Omega C_{DA}/C_D^0$ were linear (Figs. 1, 2 and 3) with a slope $-K_1/(1+K_1C_A^0)^2$ and intercept $K_1C_A^0/\alpha(1+K_1C_A^0)^2$. The values of K_1 and α given in Table 1 were calculated by the method of least-squares.

*To whom all correspondence should be addressed.

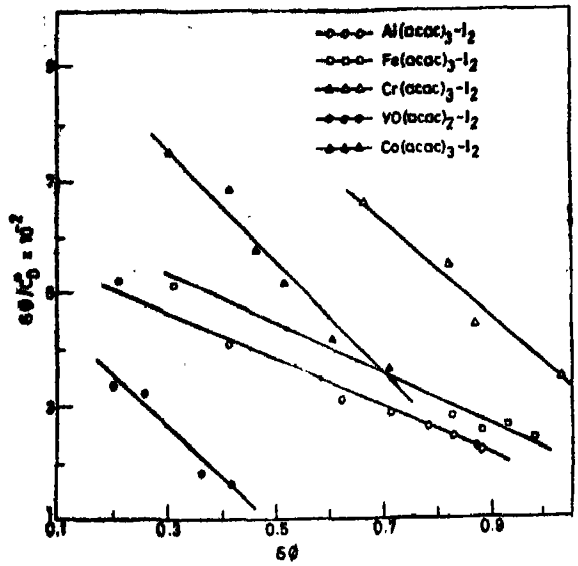


Fig. 1. Plots of $\delta\phi$ *vs* $\delta\phi / C_D^0$ for molecular complexes of metal acetylacetonates with iodine in carbon tetrachloride.

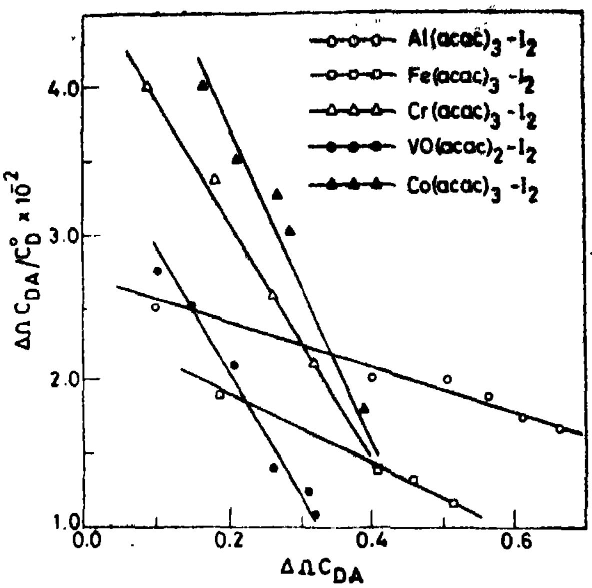


Fig. 3. Plots of $\Delta\,\Omega\,C_{DA}$ *vs* $\Delta\,\Omega\,C_{DA}/C^{\circ}_D$ for molecular complexes of metal aceytlacetonates with iodine in carbon tetrachloride.

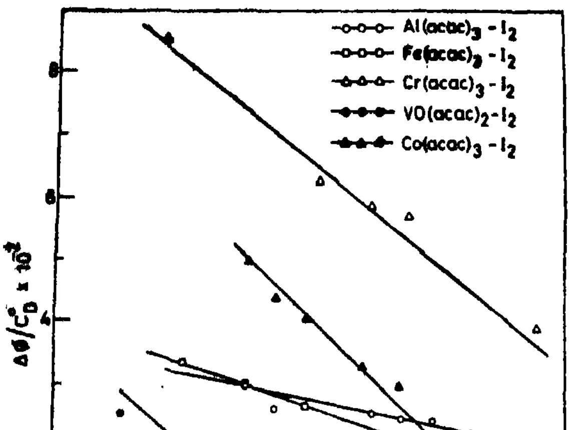


Fig. 2. Plots of $\Delta\phi$ *vs* $\Delta\phi / C_D^0$ for molecular complexes of metal acetylacetonates with iodine in carbon tetrachloride.

Results and Discussion

In order to calculate the equilibrium constants (K_1) through equations (1, 2 and 3), the refractive indices of solvent, acceptor, donor and solution (donor + acceptor) were first observed. The refraction per cm³ of solvent (ϕ_0), acceptor(ϕ_A), donor(ϕ_D) and solution(ϕ) were then calculated as reported earlier[10,11]. The difference in refraction per cm³ of solution and solvent ($\delta\phi$), solution and acceptor ($\Delta\phi$), and the refraction per cm³ due to charge-transfer complex ($\Delta\Omega C_{DA}$) have been calculated by equations(4, 6). An appreciable increase in $\delta\phi$ and $\Delta\phi$ was noticed with the increase of donor concentration and keeping the acceptor concentration constant. At this stage one may doubt, that the relative increase in $\delta\phi$ and $\Delta\phi$ may be due to the increase in donor concentration and not due to charge-transfer interaction. This problem has been solved by taking the refractive indices of donor and acceptor seperately (as C_A^0 is constant throughout the experiment) and calculating ϕ_A and ϕ_D. On mixing 1 ml ($10^{-1} - 10^{-3}M$) of donor and 1 ml ($10^{-3} - 10^{-4}M$) of acceptor, the refractive indices (n) of the solution or ϕ, the refraction per cm³ of solution increases appreciably with respect to that of seperate component. This relative increase in ϕ has been interpreted due to charge-transfer interaction between the donors and acceptor, and it is not due to increase in donor concentration. This appreciable increase in $\delta\phi$ or $\Delta\phi$ may be interpreted due to the charge-transfer from the π-orbital of benzenoid ring of metal acetylacetonates to the σ^*-orbital of iodine[1].

The equilibrium constant (K_1) and extent of electronic polarizability (α) for $M(acac)_n - I_2$ complexes are listed in Table 1. The interaction of $Ni(acac)_2$ and $Cu(acac)_2$ with iodine was also investigated but due to the low solubility of these chelates in carbon tetrachloride and limited accuracy ($\pm$ 0.0002) of the refractometer, it was not possible to get appropriate variation in the scale. It was, therefore, not possible to calculate equilibrium data (K_1 and α) for these systems. From Table 1, it is clear that the increase in the strength of molecular complexation is in the order of $Be(acac)_2 < Al(acac)_3 < Fe(acac)_3 < Cr(acac)_3 < VO(acac)_2 < Co(acac)_3$. The equilibrium constant data obtained by refractometric methods are comparable with those of spectrophotometric[1] and conductometric[2] values. Further, it is apparent that data obtained from

TABLE 1—EQUILIBRIUM CONSTANT (K_1), EXTENT OF ELECTRONIC POLARIZATION (α) DATA FOR 1:1 MOLECULAR COMPLEXES OF SOME METAL ACETYLACETONATES WITH IODINE IN CARBON TETRACHLORIDE.

Complex	Equilibrium constant*(K_1), l. mole^{-1}					Extent of electronic polarization* (α), α × 10^4		
	Spectro-photometric method[1]	Conduct-ometric method[8]	Refractometric method					
			From Eq. (1)	From Eq. (2)	From Eq. (3)	From Eq. (1)	From Eq. (2)	From Eq. (3)
$Be(acac)_2$-I_2	12.30	17.80	41.66	37.03	20.00	11.76	12.31	12.41
$Al(acac)_3$-I_2	171.20	169.00	384.61	238.09	172.41	0.74	0.64	0.75
$Fe(acac)_3$-I_2	—	—	454.54	344.82	256.41	0.75	0.83	1.04
$Cr(acac)_3$-I_2	—	888.80	909.09	800.00	833.33	0.91	0.89	1.63
$VO(acac)_2$-I_2	—	—	952.38	909.09	952.38	1.740	1.51	2.31
$Co(acac)_3$-I_2	—	1666.00	1052.63	952.38	1176.47	1.141	1.70	2.76

* A standard deviation of about ± 10-15% in these values has been estimated.

equation (3) are quite comparable with the spectrophotometric values (Table 1) than equations (1 and 2). Thus in order to get best values, one should use the equation (3) instead of equations (1 and 2). Equations (1 and 2) can be used to get qualitative values of equilibrium constants of molecular complexes. The extent of electronic polarizabilities (α) have been found increasing with the increase of equilibrium constants (K_1) except for $Be(acac)_2-I_2$ complex. Because of the limited accuracy of the instrument (± 0.0002), it was necessary to raise the concentration of solute ($10^{-2}M$) in order to get appropriate variation in the scale. At this large concentration, the values of K_1 and α are less reliable due to the self association of the solute.

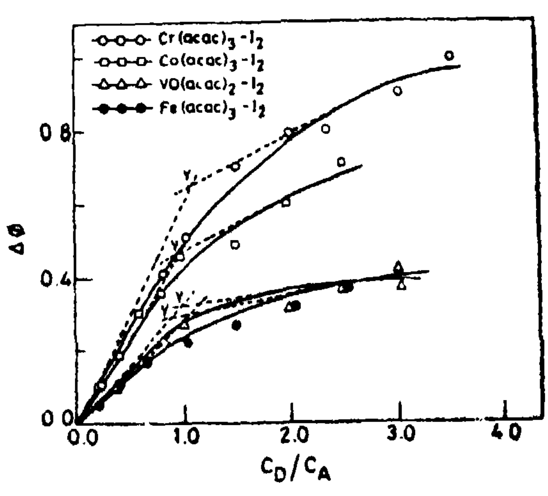


Fig. 4. Refractometric titration curve for the molecular complexes of metal acetylacetonates with iodine showing 1:1 stoichiometry.

The stoichiometry of the above mentioned molecular complexes has been determined using refractometric titration technique. Through this technique, the change in the refractometric permittivity ($\Delta\phi$) of a solution of one component (acceptor) on addition of successive amount of the other component (donor), has been measured. Now considering the addition of a dipolar donor to a non-dipolar acceptor producing a complex with a refractive index larger than the refractive index of the donor. The addition of a small amount of donor generates an equal amount of complex. The permittivity increase on successive additions of the donor and continues to increase until the equivalent quantities of the donor and acceptor are present. This situation is schematically shown by line XY of Fig. 4 which indicates 1:1 stoichiometry of these complexes.

The formation of above molecular complexes thus provides further support on the pseudo-aromatic character of metal acetylacetonate chelate rings.

Acknowledgement

One of us (R. V.) is thankful to CSIR, New Delhi for the award of Junior Research Fellowship. The authors are grateful to Professor P. C. Nigam (I.I.T., Kanpur) for providing facilities of refractometric measurements.

References

1. P. R. SINGH and R. SAHAI, *Aust. J. Chem.*, 1970, 23, 269.
2. V. N. BADONI, "Studies on the molecular complexes in metal acetylacetonates", Ph.D. Thesis, (Kanpur University, Kanpur), 1977.
3. R. SAHAI and V. N. BADONI, *Indian J. Chem.*, 1978, 16A, 1060.
4. A. ARCH and R. C. YOUNG, *Inorg. Synth.*, 1946, 2, 17.
5. R. E. ROWE and M. M. JONES, *Inorg. Synth.*, 1957, 5, 114.
6. R. C. YOUNG, *Inorg. Synth.*, 1946, 2, 25.
7. B. E. BRYANT and W. C. FERNELIUS, *Inorg. Synth.*, 1957, 5, 188.
8. N. V. SIDGWICK, Chemical elements and their compounds. (Oxford University Press, London), 1950.
9. R. COOPERATEIN, *Inorg. Synth.*, 1946, 5, 130.
10. R. SAHAI, P. C. PANDE and V. SINGH, *Indian J. Chem.*, 1979, 18A, 217.
11. R. SAHAI and V. SINGH, *Indian J. Chem.*, in press.
12. R. SAHAI, V. SINGH and REKHA VERMA, *Bull. Chem. Soc. Japan*, in press.

J. Indian Chem. Soc.,
Vol. LVII, May 1980, pp. 497-499

pH-metric, Spectral, Magnetic and Thermal Investigation on Ni-2-hydroxy-3-(3-methyl-2-buteny)-1, 4-naphthoquinone (Lapachol) Complex

S. S. SAWHNEY and S. D. MATTA

Chemistry Department, D.A.V. (P.G.) College, Dehradun (U.P.)

Manuscript received 5 May 1979, accepted 22 December 1979

$Ni(C_{15}H_{13}O_3)_2 \cdot 2\frac{1}{2}H_2O$, the nickel-lapachol complex based upon *p*H-metric, thermal studies is paramagnetic (μ_{eff} =4.5 B.M.) and non-electrolytic in nature. The protonation constant of lapachol and stability constants of nickel complex at 20° and 40° have been determined, employing Irving-Rossotti technique. The thermodynamic parameters are also reported. Spectral data suggest the participation of hydroxyl and carbonyl groups in complexation.

Desolvation of hydrated nickel-lapachol chelate, studied employing D.T.A. curve and Borchardt and Daniels equation is kinetically first order reaction. Activation energy of solid state reaction is 4250 cals/mole.

METAL complexes of lapachol are little studied[1]. Sawhney and Vohra[2] investigated recently indicator properties of lapachol. *p*H-metric, magnetic, spectral and thermal studies of nickel complex are reported in this communication.

Experimental

All the inorganic chemicals were of analytical grade. Lapachol was obtained from M/s Aldrich Co., U.S.A. Approximately 0.1*M* $NiCl_2$ was prepared in water and standardised complexometrically. Lapachol (0.01*M*) solution was prepared by dissolving weighed amount of it in Et.OH. All *p*H measurements were made with Backman *p*H-meter. Correction for 50% Et.OH-water system was applied due to Uitert and Hass[3]. For practical proton ligand stability constant(P_kH) and stability constants of the complex, three solutions (total volume 50 ml) were *p*H-metrically titrated with 0.02*M* KOH at 20° and 40° at μ=0.2*M* KCl. 50% Et.OH-water system was kept as medium.

(i) $4.00\times10^{-3}M$ HCl. (ii) $4.00\times10^{-3}M$ HCl., $1.00\times10^{-3}M$ Lapachol

(iii) $4.00\times10^{-3}M$ HCl., $1.00\times10^{-3}M$ Lapachol., $2.00\times10^{-3}M$ Ni^{2+}

Also different metal ligand molar ratio of 0:1, 1:1, 1:2 and 1:3 were titrated to arrive at certain composition of complex.

The magnetic susceptibility measurement was carried out on Cahn Faraday Magnetic Susceptibility Electrobalance (Model 7550, Calif., U.S.A.). Mercuric tetrathiocyanato(II) was used as calibrant. The manually operated thermogravimetric measurement apparatus was used. The thermogram, heating rate being fairly constant approximately 7°/minute, of the complex was obtained by using sample of air dried complex. Calcium oxalate was used as calibrant. For D.T.A. of nickel-lapachol complex, Differential Thermal Apparatus (D.T.A-2 Universal), (Manufacturers-VEB Laborelakstre 5, G.D.R.) was used for analysis. The i.r. spectra in KBr pellet was recorded on Perkin Elmer Infracord Spectrophotometer. For C. H. analysis, thermo electric equipment (THERELEK) was employed.

Isolation of complex :

Lapachol solution prepared in one equivalent KOH was added slowly with constant stirring to solution containing nickel ions. The red precipitate was filtered, washed with ice-cooled water and dried at 60-70°.

Complex	C%	H%	Ni%
$Ni(C_{15}H_{13}O_3)_2 \cdot 2\frac{1}{2}H_2O$	61.46 (61.96)	5·29 (4.94)	10.02 (11.22)

Experimental data are given in parentheses.

Results and Discussion

Nickel-lapachol complex is powder in solid state, slightly soluble in water and ethanol. It is an indication

that the complex is not polymeric like those of naphthazarin and 2,5-dihydroxy-*p*-benzoquinone[4,5].

Values of formation functions $\bar{n}_A$, $\bar{n}$ and pA were calculated using expressions given by Irving and Rossotti[6]. Plot of $-\log \frac{\bar{n}_A}{1-\bar{n}_A}$ versus *p*H yielded the value of P_kH. The metal ligand stability constants have been obtained by the methods of use of mid point, correction term[7]. To minimise the error, the method of interpolation at half $\bar{n}$ values[8] was avoided as the difference between $\log k_1$ and $\log k_2$ was less than 2.5. The values of overall changes in free energy $\triangle G°$, enthalpy $\triangle H°$ and entropy $\triangle S°$ have been determined by using wellknown temperature coefficient and Gibb's Helmholtz equation. Table I incorporates the values of P_kH, $\log k_1$, $\log k_2$ and $\log \beta_2$ and thermodynamic functions. The free energy of formation ($\triangle G°$) of complex have more negative value with the increase of temperature, indicating that complex formation is a spontaneous process. The enthalpy is negative for complex which is favourable for the formation of the complex. $\triangle S°$ is +ve, favouring the complex formation.

Table 1—Protonation constant of Lapachol, Stability constants and Thermodynamic functions of Nickel-lapachol Complex

Protonation constant/ stability constant		Temperature (°c) 20	40	$\triangle G°$ (Kcals/mole) 20°C	40°C	$\triangle H°$ (Kcals/ mole)	$\triangle S°$ (cal/mole/°c) 40°C
Log P_kH		6.45	5.69				
Log k_1	A	4.16	3.99				
	B	3.87	3.81				
	C	(4.02)	(3.90)				
Log K_2	A	3.51	3.65				
	B	3.81	3.21				
	C	3.16	3.47				
Logk_1/k_2	C	+0.86	+0.43				
Log β_2	A	7.67	7.64	−10.28	−10.96	−0.63	+33.05
	B	7.68	7.02				
	C	7.18	7.39				

A = "Correction Term" method

B = Use of mid-point method

C = Method of Interpolation at half $\bar{n}$ values

The value of $\bar{n}$ approaches 2 for the complex. It indicates the existence of 1:1 and 1:2 complexes. *p*H-metric titrations of different metal-ligand molar ratio of 0:1, 1:1, 1:2 and 1:3 show that the reaction between nickel and lapachol takes place with the liberation of protons, the limiting condition being reached with metal-ligand molar ratio of 1:2. Afterwards overlapping of curves takes place, indicating that a maximum of two protons can be liberated in the reaction per metal ion. This supports the existence of 1:2 metal to ligand complex.

With the appearance of broad absorption band in the spectra of complex, in the 3400 cm^{-1} range, indicative of O-H stretching, presence of lattice water was concluded. Further it has been seen that the strongest peak at 1655 cm^{-1} (>C=O) is shifted below showing, thereby, the participation of carbonyl group in complexation. Nickel lapachol complex is paramagnetic (μ = 4.5 B.M). Probably it is a tetrahedral complex as all those complexes in which ligands are identicals have moments of 3.7−4.0 B.M.

T.G. and D. T. A. studies are very informative. For nickel lapachol complex (Fig. 1), it would appear from T.G. curve that it is stable upto 80° and loses $2\frac{1}{2}$ H_2O from 80° to 140°. Plateau between 140° and 168° corresponds to $Ni(C_{15}H_{13}O_3)_2$. Further dissociation starts from 168° and completes until 540°; that plateau between 540° and 740° points to nickel oxide.

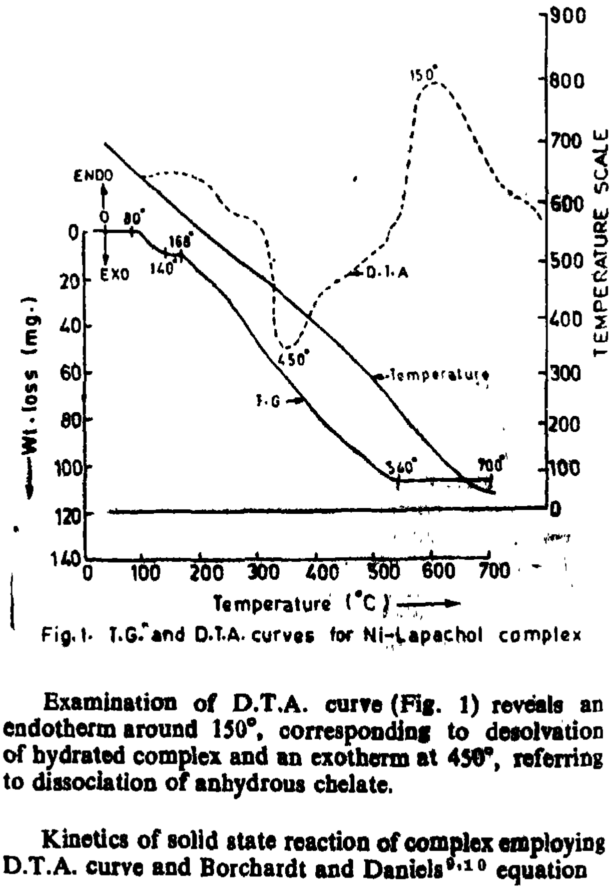


Fig. 1. T.G. and D.T.A. curves for Ni-Lapachol complex

Examination of D.T.A. curve (Fig. 1) reveals an endotherm around 150°, corresponding to desolvation of hydrated complex and an exotherm at 450°, referring to dissociation of anhydrous chelate.

Kinetics of solid state reaction of complex employing D.T.A. curve and Borchardt and Daniels[9,10] equation

$$k = h'/A\text{-}a$$

where, A = Total area under D.T.A. curve,

a = Area at time, t,

h′ = Height of curve at time, t,

k = Specific rate constant,

have been studied.

Desolvation of hydrated complex :

$$Ni(C_{15}H_{13}O_2)_2 \cdot 2\tfrac{1}{2} H_2O\,(S) \xrightarrow{\text{heat}} Ni(C_{15}H_{13}O_2)_2\,(S) + 2\tfrac{1}{2} H_2O\,(\text{vapour})$$

is of first order[11,12]. Plot of lnk (calculated with Borchardt and Daniels equation) versus the reciprocal of absolute temperature yielded a straight line, confirming thereby the reaction under investigation to be of first order reaction. Activation energy of the reaction calculated from the slope of the curve is 4250 cals/mole (Fig. 2).

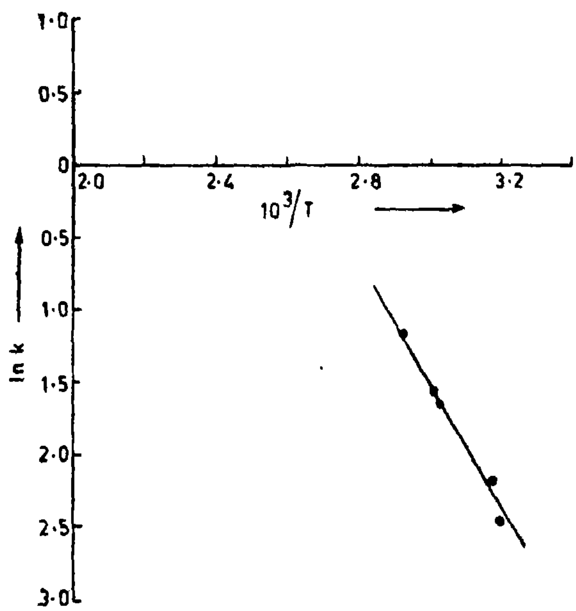


Fig. 2. Borchardt and Daniel's Plot.

Acknowledgement

The authors express their thanks to Shri N. S. Verma, Principal and Dr. P. K. Sharma, D.A.V.(P.G.) College, Dehra Dun for necessary facilities.

References

1. A. DUFRESNE, C. G. DELIMA, J. KRUDSEN and J. E. MARCINA, *J. Inorg. Nuclear Chem.*, 1973, **35**, 789.
2. S. S. SAWHNEY and NEELAM VOHRA, *J. Indian Chem. Soc.*, 1977, **54**, 403.
3. L. G. VAN UITERT and C. G. HAAS, *J. Amer. Chem. Soc.*, 1953, **75**, 451.
4. R.S. BOTTEI and T.F. FANGMAN, *J. Inorg. Nuclear Chem.*, 1966, **28**, 1259.
5. R. S. BOTTEI and P. L. GERACE, *J. Inorg. Nuclear Chem.*, 1961, **23**, 245.
6. H. M. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.*, 1954, 2904.
7. H. M. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.*, 1953, 3397.
8. J. BJERRUM, "Metal Ammine Formation in Aqueous Solution", P. Hasseand Son, Copenhagen, 1941, 298.
9. K. B. YATSIMIRSKII, "Instability constants of complex compounds, Van Nostrand, New York, 1963, 63.
10. H. J. BORCHARDT and F. DANIELS *J. Amer. Chem. Soc.*, 1957, **79**, 41.
11. W. W. WENDLANDT, "Techniques of Inorganic Chemistry", H. B. JONASEEN and A. Weissberger, Eds., Interscience, New York, 1963, Vol. I, 209.
12. W. W. WENDLANDT, *J. Amer. Educ.*, 1961, **38**, 571.

J. Indian Chem. Soc.,
Vol. LVII, May 1980, pp. 500-502

Heterocyclic Azo Dyes as the Chromogenic Reagents for the Extraction-Photometric Determination of Silver(I)

ISHWAR SINGH*, YASHBIR S. VARMA, J. L. SHARMA, B. S. GARG and R. P. SINGH

Department of Chemistry, University of Delhi, Delhi-110 007, India

Manuscript received 4 May 1979, revised 27 October 1979, accepted 18 March 1980

Silver(I) interacts with 1-(2-quinolylazo)-2-acenaphthylenol (QAAc) and 1-(2-lepidylazo)-2-acenaphthylenol (LAAc) to give red coloured (1:1) water-insoluble complexes at moderately alkaline pH's. The complexes are extractable in various water-immiscible organic solvents and exhibit maximum absorbance at 540-45 nm. The Sandell's sensitivity of the colour reaction is 0.0052 μg Ag/cm² ($\epsilon = 2.08 \times 10^4$) for silver-QAAc complex and 0.0037 μg Ag/cm² ($\epsilon = 2.88 \times 10^4$) for silver-LAAc complex. The reagents have been found to be fairly selective for the determination of silver(I) in presence of various interfering base metals.

A few reagents are known for the spectrophotometric determination of silver ions. The extractive dithizone method, and the rhodamine method, are of particular importance[1,2]. A little information has been given about a few heterocyclic azo dyes[3]. A method of determination of silver with PAR[4] has been reported. 1-(2-Quinolylazo)-2-acenaphthylenol (QAAc) has already been used for the spectrophotometric determination of various metal ions[5-7]. In the present communication, the use of QAAc and another azo dye, 1-(2-lepidylazo)-2-acenaphthylenol (LAAc) has been explored for the spectrophotometric determination of silver.

Experimental

Reagents: A stock solution of silver (I) was prepared by dissolving appropriate amount of silver nitrate (reagent grade) in double distilled water. QAAc was synthesized[8] and its stock solution was prepared by dissolving appropriate amount (0.323 g/l for $10^{-3} M$) in pure methanol. LAAc was synthesized by coupling 1, 2-acenaphthaquinone with 2-hydrazinolepidine (obtained by refluxing 2-chlorolepidine[9] with hydrazine hydrate) in methanolic medium. Purity of the reagent was checked by t.l.c. and its stock solution was prepared in pure methanol (0.337 g/l for $10^{-3} M$). A few drops of pure chloroform can be added, if necessary, to the reagents before dissolving them in methanol, as these are highly soluble in chloroform. In no case reagent solutions older than four days were used.

Dilute solutions of hydrochloric acid, sodium acetate and sodium hydroxide were used for pH adjustments.

Phosphate-sodium hydroxide buffer was used for adjustment of pH around 10.0.

Apparatus: A Unicam SP-600 spectrophotometer with 10 mm matched glass cells was used for absorbance purposes.

A Beckman pH meter model Expandomatic SS-2, with a saturated calomel and glass electrode assembly was used for pH measurements.

Recommended Procedure: To a suitable aliquot containing 11 to 40 μg of silver(I), add sufficient excess of QAAc solution or to a suitable aliquot containing 12 to 37 μg of silver (I), add sufficient excess of LAAc solution, followed by 2.0 ml of phosphate/hydroxide buffer (pH ~ 10.0). Raise the volume to 10 ml keeping 50% (v/v) methanol—aqueous medium. Keep for two minutes and extract in 10 ml of freshly distilled chloroform. Measure the absorbance at λ_{max} (540-45 nm) against a reagent blank prepared under identical conditions. The amount of silver can be deduced from the calibration curve drawn under similar conditions.

Results and Discussion

Addition of methanolic solution of reagent (QAAc or LAAc) to a very dilute aqueous solution of silver(I) resulted a water-insoluble red precipitate in moderately alkaline medium, which was soluble when methanolic concentration was kept more than 75% (v/v). The precipitate was extractable in various water-immiscible organic solvents, however, chloroform or carbon tetrachloride was used for extraction purposes, as the absorbance was maximum in these and the complexes were stable at least 4 hrs.

Spectral characteristics of the complexes:

A series of solutions containing silver(I) ($2 \times 10^{-5} M$) and the reagent QAAc or LAAc ($2 \times 10^{-4} M$) at

* Present address: Department of Chemistry, M. D. University, Rohtak-124 001 (India).

different pH were prepared keeping 50%(v/v) methanolic concentration and extracted in 10 ml of freshly distilled chloroform. Their spectra were recorded against a reagent blank. At all pH levels both the complexes had maximum absorbance at 540- 5 nm.

Effect of pH :

The complexes exhibited constant and maximum absorbance in the pH range 8.5 – 10.7 when QAAc was used and 9.0 – 10.1 when LAAc was used. A phosphate/hydroxide buffer of appropriate pH (~10.0) was used during further studies.

Effect of Reagent Concentration :

Absorbance data recorded for a series of solutions containing silver(I) ($2 \times 10^{-5} M$) and varying amounts of reagent (at pH~10.0) showed that 30 molar times of QAAc or 20 molar times of LAAc are required for full colour development of the complexes.

Other Physico-Chemical Characteristics :

Validity of Beer's law and optimum range for accurate determination of metal ions at a pH of 9.5± 0.5, determined by Ringbom plots, are 0 – 4.2 ppm and 1.1 – 4.0 ppm respectively for silver-QAAc complex and 0 – 4.6 ppm and 1.2 – 3.7 ppm respectively for silver-LAAc complex. The Sandell's sensitivity of the colour reactions calculated from Beer's law plots comes out to be 0.0052 μg Ag/cm² ($\epsilon = 2.08 \times 10^4$ 1.mole⁻¹ cm⁻¹.) for silver-QAAc and 0.0037 μg Ag/cm² ($\epsilon = 2.88 \times 10^4$ 1.mole⁻¹cm⁻¹) for silver-LAAc complex at their λ_{max}.

Composition of the Complexes :

Composition of the complexes was determined by making use of Job's method of continuous variation. Results obtained showed that the metal ion and reagent interact in 1:1 ratio in both the cases.

Absorbance Deviations :

Measured under the experimental conditions, the mean absorbance of eight solutions containing 1 ml of $2 \times 10^{-4} M$ silver was found to be 0.415, with a standard deviation of 0.005 for silver-QAAc complex and the mean absorbance was 0.576 with a standard deviation of 0.043 for silver-LAAc complex.

Effect of Diverse Ions :

The effect of diverse ions was studied, taking 2.16 μg/ml of silver(I), adding different amounts of diverse ions and determining the amounts of silver content following the recommended procedure. It was found that lanthanides (15-fold each), In(III), Mn(II), Fe(II) and (III), Au(III), platinum metals in cold except Pd(II) (5 fold each) did not interfere. However, I^-, CNS^-, CN^-, $S_2O_3^{2-}$, thiourea, Zn(II) interfere seriously. The amounts of other ions (in ppm), which did not cause deviation of more than ± 3% in absorbance are given below :

PO_4^{3-}, BO_3^{3-} (1000) ; oxalate, citrate, tartrate (500) ; F^-, Cl^-, NO_3^-, SO_4^{2-} (200), Br^-, SO_3^{2-} (100) ; Cd(II), Hg(II), Cu(II) Co(II), Ni(II) (5, masked with oxalate or citrate). Pd(II) (4, masked with nitrite).

Conclusion :

Dithizone and dimethylaminobenzylidenerhodanine have been shown to be the most useful reagents for silver[1,2], but neither of them is specific. Silver is determined with dithizone by the monocolour, mixed colour and extractive titration methods. In case of rhodanine method, the absorbance of the complex formed, depends on the acidity of the solution, the concentration of rhodanine and time. The optimum acidity corresponds to 0.05*M* HNO_3 and at the optimum rhodanine concentration (0.001 – 0.002%), maximum absorbance is obtained in 5 min ; the colour fades after this. The temperature is also kept constant since large variations affect the colour intensity. In

TABLE 1—SENSITIVITIES OF SOME METHODS FOR DETERMINATION OF SILVER

Reagents	Sensitivity (μg Ag/cm² for log Io/I=0.001)	Reference
Dithizone (mixed colour)	0.01 (yellow filter)	1
p-Dimethylaminobenzylidenerhodanine (direct)	0.005/495 nm	1
p-Dimethylaminobenzylidenerhodanine (indirect)	0.0026/460 nm	1
Bromopyrogallol red	0.0034/590 nm	10
Methyl phenyldimercaptothiopyrone	0.014/510 nm	11
Thiodibenzoylmethane (C_6H_6)	0.01/420 nm	12
4-(2-Pyridylazo) resorcinol	0.0054/510 nm	4
1-(2-Quinolylazo)-2-acenaphthylenol (QAAc)	0.0052/540 nm	present method
1-(2-Lepidylazo)-2-acenaphthylenol (LAAc)	0.0037/540 nm	„

practical analysis, the separation of silver from the other metals is required before applying either of the method mentioned above. Gold and palladium react with both the reagents and cause interference. Small amounts of mercury(II) can be tolerated in direct rhodanine method but not in the dithizone method. Dagnall and West[10] recommended pyrogallol red and bromopyrogallol red methods, in which the cationic complex of silver with 1,10-phenanthroline reacts with the reagents to yield an ion-association complex. Among the heterocyclic azo dyes, only the colour reactions with PAN, *p*-PAN and 7-(2-pyridylazo)-8-quinolinol have been reported[3], but details are lacking. However, PAR[4] has been shown to be a sensitive reagent for silver. The present methods are direct and rapid. The complexes formed are fairly stable at least for 4 hrs and the colour intensity is not affected by heat. The reagents have been found to be sensitive as well as selective as many of the interfering cations could be masked with complexing anions like oxalate and citrate. The sensitivities of the colour reactions are compared with some other well known reagents reported for silver in Table 1.

References

1. E. B. SANDELL, Colorimetric Determination of Traces of Metals", Interscience Publishers, Inc. N. Y., 1959.
2. I. M. KOLTHOFF and P. J. ELVING, "Treatise on Analytical Chemistry", Interscience Publishers, Inc. N. Y., 1966, Part II, Vol. 4.
3. H. A. FLASCHKA and A. J. BARNARD, JR., "Chelates in Analytical Chemistry", Marcel Dekker, Inc., N.Y., 1972, Vol. 4.
4. M.C. ESHWAR and B. SUBRAHAMANYAM, *Z. Anal. Chem.*, 1974, 272, 44.
5. ISHWAR SINGH, Y. L. MEHTA, B. S. GARG and R. P. SINGH, *Talanta*, 1976, 23, 617.
6. ISHWAR SINGH, B. S. GARG and R. P. SINGH, *Z. Anal. Chem.*, 1977, 284, 42.
7. ISHWAR SINGH, B. S. GARG and R. P. SINGH, *J. Indian Chem. Soc.*, 1977, 54, 787.
8. Y. L. MEHTA, B. S. GARG and R. P. SINGH, *Curr. Sci.*, 1974, 43, 11.
9. C. E. KASLOW and W. M. LAUER in E. C. HORNING, Editor-in-Chief, "Organic Synthesis", John Wiley & Sons, Inc., N. Y., London, 1960, Collective Vol. 3, p. 194.
10. R. M. DAGNALL and T. S. WEST, *Talanta*, 1961, 8, 711; 1964, 11, 1533, 1627.
11. A. M. ARISKEVICH, Y. I. USATENKO, A. A. KROIK, L. F. D'YACHENKO, V. V. VOLOSHINA and T. V. ZAMOVSKAYA, *Anal. Tekhnol Blagorod. Metal.*, 1971, 194; *Chem. Abs.*, 1973, 78, 11121b.
12. R. R. MULYE and S. M. KHOPKAR, *Anal. Chim. Acta*, 1975, 76, 204.

J. Indian Chem. Soc.,
Vol. LVII, May 1980, pp. 503-505

Synthesis and Thermolysis of Possible Laser Material—Part I

H. SINGH* and U. K. RATHI

Chemica Laboratories, D. S. College, Aligarh-202 001

Manuscript received 24 September 1979, accepted 30 December 1979

Substituted ortho-hydroxy chalcones and acetophenone have been used as a co-ordinating ligand. The complex compounds of the ligands with Y(III), La(III), Pr(III) and Nd(III) have been isolated and characterized on the basis of elemental analyses and from the thermolysis.

LASER technology as an unique tool has enticed the scientist of prevailing era to explore new laser material[1,2]. The efficiency of chalcones[3-7] (Ar–CO-CH=CH–Ar'), and acetophenones[8-11] (Ar–CO–CH_3), have captivated us to synthesise the new laser material as reported by Charles[12], Patel[13] and Garg[14]. The chalcones have been prepared and have been introduced for the first time in the literature for the complexation of Y(III), La(III), Pr(III) and Nd(III). An idea smote to prepare the complexes of these metal ions with 2-hydroxy-5-bromo acetophenone, 2'-hydroxy-4'-methyl chalcone, 2'-hydroxy-4'-methyl-5'-chloro chalcone, 2'-hydroxy-5'-chloro chalcone and 2'-hydroxy-5'-bromo chalcone. The present manuscript is a part of our comprehensive study during the investigation of these complexes as laser material.

Experimental

2-Hydroxy-5-bromo acetophenone (HBA); m.p. 62°, was prepared as Noris and Sturgies[15] and 2'-hydroxy-4'-methyl chalcone (HMC); m.p. 88.5°, 2'-hydroxy-4'-methyl-5'-chloro chalcone (HMCC); m.p. 141°, 2'-hydroxy-5'-chloro chalcone (HCC); m.p. 108° and 2'-hydroxy-5'-bromo chalcone (HBC); m.p. 107-8° were prepared by the method of Kerrer *et al*[16].

The solutions of rare earth chlorides of AnalaR grade and ligands were prepared in ethanol. The thermogravimetric data have been recorded by programming the furnace temperature at the rate of 5° per minute and thermograms were plotted between temperature and percentage of weight loss of the complexes.

Preparation of Complexes:

To a solution of 0.005 mole of rare earth chloride, the 0.017 mole of ligand solution was added with vigorous stirring. On addition of 1 : 20 (water : ammonia) mixture, the precipitation of Y(IIII), La(III), Pr(III) and Nd(III) complexes were obtained. The complexes were washed with hot ethanol-water mixture and then dried in an oven at 110°.

The percentage of metal in the complex was determined by heating and igniting the complex to its oxide The oxide was dissolved in hydrochloric acid and titrated against EDTA using xynol orange indicator at *p*H 6 to find out the metal content.

The characteristic data of aforesaid complexes are tabulated in the Table 1.

Result and Discussion

The elemental analysis of the complexes correspond with the stoichiometry 1 : 3 between metal and ligand in each complex. These complexes are non-electrolytic in nature and show the inert behaviour towards all common organic solvents.

Thermolysis of Y(III), La(III), Pr(III) and Nd(III) complexes with HBA:

The typical thermogravimetric curves (Fig. 1) for the samples of the $Ln(HBA)_3$; Ln=Y(III), La(III), Pr(III) and Nd(III) system show the rapid decomposition in the region 200-400°. This is in agreement with the reported work on the rare earth acetoacetanilide[17]. The order of decreasing heat stability was Y(III) > La(III) > Pr(III) > Nd(III). The carbonaceous residue which remains unchanged at 740° contains all the metal initially present in the complexes, suggesting non-volitilization of the chelates under the experimental conditions. Weight loss above 400° can only be due to the pyrolysis of the initially formed decomposition products. Weight loss below 200° most likely represent

*To whom all correspondence should be made.

TABLE 1—PHYSICAL CHARACTERISTICS—RARE EARTH CHELATES

Complex	Colour	Elemental Analyses %					
		Carbon		Hydrogen		Metal	
		Found	Calcd.	Found	Calcd.	Found	Calcd.
Y(III)-HBA	Greenish Yellow	39.18	39.40	2.40	2.46	12.30	12.16
La(III)-HBA	,,	36.84	36.87	2.28	2.30	18.00	17.78
Pr(III)-HBA	,,	36.84	36.78	2.48	2.29	18.28	17.99
Nd(III)-HBA	,,	36.70	36.62	2.28	2.28	18.48	18 34
La(III)-HMC	Yellow	67.72	67.77	4.70	4.58	16.17	16.34
La(III)-HMCC	Orange-Yellow	60.70	60.41	3.49	3.77	14.29	14.57
La(III)-HCC	,, ,,	58.98	59.24	3.48	3.29	15.41	15.24
La(III)-HBC	,, ,,	51.58	51.67	2.93	2.87	13.33	13.29

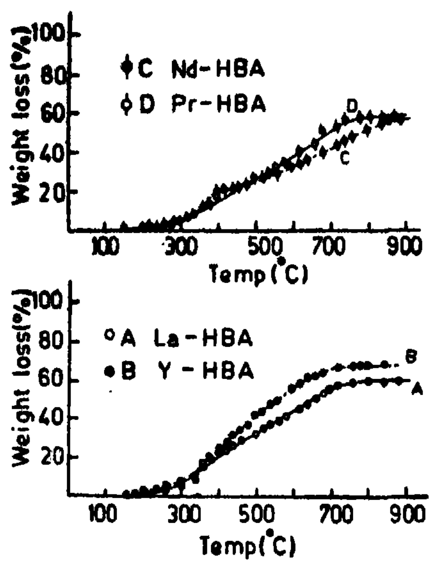


Fig. 1

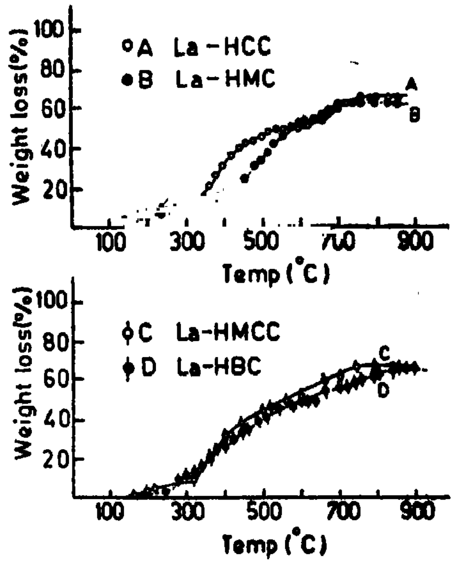


Fig. 2

either slow decomposition or the loss of small amount of adhered ligand. The weight of metals calculated from the weight of the oxides(Y_2O_3, La_2O_3, Pr_2O_3 and Nd_2O_3) remaining when the residue from the thermogravimetric runs were reheated to 750° or above, also confirms the stoichiometric composition of $Ln(HBA)_3$. Since it is very difficult to precipitate these metals with HBA quantitatively, therefore, the thermogravimetric estimation can not be recommended for determining the lanthanones.

Thermolysis of La(III) complexes with chalcones :

The lanthanum complexes with chalcones viz., HMC, HMCC, HCC and HBC, were put for TGA to decide the effect of ligand on the nature of thermograms. The rapid decomposition in the region 200-400° is also shown by the pyrolysis curve (Fig. 2) of these complexes.. The thermal stability of lanthanum complexes is inversely proportional to their conversion factors (metal/metal-complex) as given in Table 2 because it is observed that the order of heat stability is La(III)-HBC (160°)>La(III)-HMCC (155°)>La(III)-HCC (145°)> La(III)-HMC (140°) ; and the conversion factors are 0.1329, 0.1457, 0.1524 and 0 1634 for the corresponding complex i.e., higher the molecular weight of the reagent, the higher is the thermal stability of lanthanum chelate.

The above results coincide with the established facts that an increase in conjugation[18] and an addition of extra aromatic ring[19] in ligand enhance the thermal stability of its chelate resulting in an increase of electron density at reactive centres[20]. The chalcone possesses $\alpha:\beta$-unsaturated carbonyl group in the conjugation of two benzene rings and consequently increases the heat stability of its metal chelate to a great extent.

TABLE 2—THERMOGRAVIMETRIC ANALYSIS DATA

Complex	Weight of sample taken mg.	Thermal stability Temp. (°C)	Decompo-sition Temp. (°C)	Approx. temp. (°C)	Possible residue	Residue % Found	Residue % Calcd.	Conversion Factor (Metal/ Metal complex)
Y(III)-HBA	85.0	165	280	760	Y_2O_3	31.76	30.89	0.1216
La(III)-HBA	180.0	160	260	750	La_2O_3	41.66	41.72	0.1778
Pr(III)-HBA	194.0	145	280	760	Pr_2O_3	41.75	42.12	0.1799
Nd(III)-HBA	299.0	140	240	840	Nd_2O_3	43.44	42.88	0.1834
La(III)-HMC	57.0	140	280	700	La_2O_3	38.59	38.33	0.1634
La(III)-HMCC	34.0	155	320	740	,, ,,	32.35	43.17	0.1457
La(III)-HCC	32.0	145	260	740	,, ,,	34.37	35.75	0.1524
La(III)-HBC	31.0	160	240	840	,, ,,	32.25	31.18	0.1329

The data from pyrolysis curves are compiled in Table 2 which conspicuously indicate about the decomposition temperature and final product (expected) left after ignition.

Acknowledgement

The authors wish to thank Agra University, Agra for the award of junior research fellowship (UGC, New Delhi) to one of them (UKR) and Dr. S. S. Gupta, D. Litt., F.R.E.S., Principal, D. S. College, Aligarh for providing the necessary facilities and constant encouragement for supplicating this work.

References

1. A. LEMPICKI and H. SAMUELSON, *Appl. Phys. Lett.*, 1963, 2, 159.
2. M. METLAY, *J. Chem. Phys.*, 1963, 39, 491.
3. A. A. EFIMOR and O. I. BETIN, *Zh. Prikl. Spectrosk.*, 1975, 23(6), 1054.
4. R. R NAIDU, *Talanta*, 1975, 22(7), 614.
5. K. SYAMSUNDER, *Proc. Indian Acad. Sci.*, 1968, 67(2), 90.
6. N. S. BIRDAR, B. R. PATEL and V. H. KULKARNI, *Inorg. Chim. Acta*, 1976, 20(3), 183.
7. V. L. SHELPIN, O. A. OSVPOR and O. E. SHELPIN, *Zh. Khim.*, 1970, 201 ; *C. A.*, 1971, 4, 213.
8. M. H. GANDHI and M. N. DESAI, *J. Micro. Chem.*, 1968, 13, 500.
9. D. P. GRADDON and G. M. MOCKLER, *Austr. J. Chem.*, 1967, 20, 21.
10. N. V. DESPANDE, M. P. SAHKARI and A. J. MUKHEDKAR, *J. Indian Chem. Soc.*, 1977, 54(4), 410.
11. R. P. SINGH, Y. DUTT and S. PRAKASH, *Indian J. Chem.*, 1971, 9(2), 165.
12. R. G. CHARLES, *J. Inorg. Nuclear Chem.*, 1964, 26, 2298.
13. J. N. PATEL and D. N. SEN, *J. Indian Chem. Soc.*, 1973, 50, 413.
14. C. L. GARG, K. V. NARASIMHAM and B. N. TRIPATHI, *J. Inorg. Nuclear Chem.*, 1971, 33, 387.
15. J. F. NORIS and B. M. STURGIES, *J. Amer. Chem. Soc.*, 1939, 61, 1413.
16. P. KERRER, Y. YEN and I. REICHSTAN, *Helv. Chim. Acta*, 1970, 13, 1308.
17. A. P. BUDHKAR, P. UMAPATHY and D. N. SEN, *Indian J. Chem.*, 1971, 9, 376.
18. R. S. BOTTEI and C. P. MCEACHERN, *J. Inorg. Nuclear Chem.*, 1970, 32, 2653.
19. R.S. BOTTEI and J.C. O'REILLY, *J. Inorg. Nuclear Chem.*, 1968, 30, 1481.
20. V. SESHAGIRI and S. BRAHAMJI, *Z. Anal. Chem.*, 1972, 262, 275.

J. Indian Chem. Soc.,
Vol. LVII, May 1980, pp. 506-512

Influence of Solvent on Reaction Rate and Mechanism

M. M. ELSEMONGY[§] and M. F. AMIRA

Chemistry Department, Faculty of Science, Mansoura University, Egypt

Manuscript received 24 September 1979, accepted 4 March 1980

A general equation for the variation of specific rate constant k with dielectric constant D for any reaction, in which the transition state may or may not be polarized and the slope of log k – D variation at any temperature may be positive or negative, has been proposed. This equation was proved to be applicable to usual reactions as well as those exhibiting minima or maxima with solvent composition variation. The best method for computation of $a_{\ddagger}$, the distance of closest approach of solvent molecules to the transition state in a biomolecular reaction, has been developed. The acid hydrolysis of propionamide has been studied, in dioxane-water solvent mixtures at five temperatures within the range 25-65°, in the light of the proposed relations. The influence of the solvent on the reaction mechanism, which explains the kinetic data, has been quantitatively studied and discussed.

RECENTLY, a method for calculating b^*, the distance of closest approach of solvent molecules to the activated complex in a bimolecular reaction has been suggested[1]. Following the method of Laidler and Landskroener[2], the relationship of k, the rate constant to both D, the dielectric constant and T, the absolute temperature for an ion-dipole type of bimolecular reaction has been expressed[1] in the general form,

$$\log k = \log k_o + \frac{X}{TD} + \frac{Y}{T}, \qquad \ldots (1)$$

where X and Y are numbers depending on the distribution of charges, the dielectric constant of solute and b^*. According to the authors treatment[1], the X value could be obtained from the slope of the linear plots of log k against 1/D and the mean value of Y between two temperatures close to the experimental temperature could be determined from the expression,

$$\log \frac{k_1}{k_2} = \left(\frac{X_1}{D_1T_1} - \frac{X_2}{D_2T_2}\right) + Y\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad \ldots (2)$$

where the terms with subscripts 1 and 2 represent their values at temperatures T_1 and T_2. Thus using the values of X and Y, the b^* values could be calculated. Those authors[1] studied the alkaline hydrolysis of ethyl acetate in DMSO-water mixtures [5–25%(v/v) of DMSO] in a very small range of dielectric constant variation (D=76.43–75.80 and 74.73–74.05 at 30.2 and 35°, respectively). Using the size of OH^- ion (3.69 Å) in aqueous medium, the average value of b^* calculated was 2.415 Å. They[1] believe their method to be quite convincing. However, in their treatment we must point out that: X and Y given in equation (1) are functions of (dependent on) solvent composition, and are not constants for different solvents at any given temperature as reported[1].

The aim of the present work is to 1) propose a more general equation for the variation of specific rate constant with dielectric constant for any reaction, 2) test the applicability of the proposed equation to usual reactions as well as reactions exhibiting minima or maxima with solvent composition variation, 3) develop the best method for computation of the distance of closest approach of solvent molecules to the transition state, and 4) discuss the role and influence of solvent on reaction mechanism.

Dioxane is completely miscible in all proportions with water. However, this property, combined with a very low dielectric constant, makes dioxane-water mixture highly suitable as solvents for the study of the reaction rates and mechanisms in media of continuously and rapidly varying dielectric constant. The acid hydrolysis of formamide[5] and acetamide[6] has been investigated in these solvents. The reaction rates were found to pass through minima with progressive addition of dioxane. In the present paper, the acid hydrolysis of propionamide in dioxane-water solvent mixtures was studied in order to apply the data thus obtained together with data in literature to verify the above mentioned aim.

Theoretical:

In recent theories of the solvent effect on reaction rates and mechanisms, the dielectric constant of the medium plays a very important role. The influence of dielectric constant on reaction velocity, at any tempera-

§ To whom correspondence should be addressed. The present address: Chemistry Department, Faculty of Science, Kuwait University, P.O. Box 5969, Kuwait.

ture, has been given by Elsemongy's equation[4],

$$k = k' \, e^{\alpha(D-1)}, \quad \ldots (3)$$

where k is the velocity constant, k' is its value at D = 1, and α is a constant. This relation predicts a linear dependence of log k on D and it was reported[4] to be valid in aqueous-organic mixed solvents over a wide range of dielectric constant. However, the plot of log k versus D for the acid hydrolysis of acetamide[7] in isopropanol-water mixtures gave two linear portions of positive slopes separated by a sharp boundary at each temperature, and it is reported[7] that Elsemongy's equation[4] is obeyed for each linear part in the alcohol- and water-rich regions. Moreover, in reactions exhibiting minima[5,6], the plot of log k versus D gave two linear portions of positive and negative slopes in the water and dioxane-rich mixtures respectively. So, at any temperature, there are two values for k' corresponding to the two linear portions in the two regions[5].

It is necessary now to propose a more general equation for the variation of specific rate constant with dielectric constant of the medium for any reaction. It has been found that the change with temperature of the dielectric constant of the pure solvents and the solvent-water mixtures may be expressed[8,9] with considerable accuracy by equation (4).

$$\log D = \log a - b\,T, \text{ or, } \log \frac{a}{D} = b\,T \quad \ldots (4)$$

where a and b are empirical constants[8,9]. Equation (4) has also been tested[8] using a number of series of data in the literature. The results indicate that equation (4) is valid[8] within the experimental errors over a temperature range of at least 150°.

Substitution of the T value from equation (4) in Arrhenius equation,

$$\log k = \log A - \frac{E}{2.3026\,R}\,\frac{1}{T} \quad \ldots (5)$$

yields,

$$\log k = \log A - \frac{E\,b}{2.3026\,R}\,\frac{1}{\log (a/D)} \quad \ldots (6)$$

Equation (6), is a general equation, represents the variation of specific rate constant at various temperatures with the corresponding dielectric constant of the medium for any solvent composition. The plot of log k against 1/log (a/D) should yield a straight line of a negative slope (-Eb/2.3026 R) and an intercept log A, for each solvent composition.

The value of k' may be obtained from equation (6) by putting D=1, thus,

$$\log k' = \log A - \frac{E\,b}{2.3026\,R}\,\frac{1}{\log a} \quad \ldots (7)$$

The value of k' varies with solvent composition and in each, it corresponds certain temperature at which D=1. Generally, the dielectric constant decreases, as the temperature rises[8,9], and reaches unity at high temperatures. If equation (4) is assumed to hold in the temperature range 0-1000°, the calculated temperatures corresponding to D=1 are shown in Table 3. Thus, the calculated k' values, from equation (7), are practically reasonable and possible at the temperatures indicated.

The relationship between k and k' can be obtained, from equations (6) and (7), by eliminating log A.

$$\log k = \log k' - \frac{E\,b}{2.3026\,R}\left(\frac{1}{\log (a/D)} - \frac{1}{\log a}\right) \quad \ldots (8)$$

This equation predicts that, at different temperatures, log k will vary linearly with 1/log (a/D) for any solvent composition, and thus the k' value can be calculated from the intercept to a good accuracy without any doubt. Equation (8) is a more general rate equation which predicts the effect of the solvent (dielectric constant) on any type of reactions, in which the transition state may or may not be polarized and the slope of log k-D variation at any temperature may be positive or negative.

Experimental

The purification of propionamide and dioxane was described[2,3] before. The preparation of solutions, kinetic procedure and the experimental details have been reported elsewhere[5]. All compositions were accurate to within ±0.02 wt %. All solutions were freshly prepared before taking measurements. The dielectric constants of dioxane-water solvent mixtures were obtained by calculation and interpolation from the data of Åkerlof[8].

Results and Discussion

The acid hydrolysis of propionamide has been studied in water and in dioxane-water mixtures (upto 60% by weight dioxane) at five temperatures within the range 25-65°. The rate constants are listed in Table 1 for various temperatures and solvent compositions. Each is the mean of at least, and generally of more than, two experiments. The values of k, the second order velocity constant are those found from the best straight line drawn through the experimental points. Rate constants were generally reproducible to within ±1%. Plots of log k against 1/T for the reaction in the different solvent mixtures gave practically good straight lines showing that the data follow Arrhenius equation very closely. The values of the activation energy, E, and frequency factor, log A, were evaluated from the least square slopes and intercepts of these lines, and are collected in Table 1.

The specific reaction rate (in liter mole^{-1} sec^{-1}) of the acid hydrolysis of propionamide in dioxane-water

TABLE 1 – VELOCITY CONSTANTS (IN LITER MOLE^{-1} SEC^{-1}), ENERGIES OF ACTIVATION (IN JOULE MOLE^{-1}) AND FREQUENCY FACTORS IN DIOXANE-WATER MIXTURES

Dioxane Wt %	10^4k 25°C	35°C	45°C	55°C	65°C	E ± 495	log A ± 0.08
0	1.0715	3.2050	8.6144	21.630	52.834	81410	9.30
5	1.0463	3.1053	8.3556	20.908	50.919	81169	9.25
10	1.0225	3.0103	8.0917	20.200	48.994	80880	9.18
20	0.9737	2.8125	7.5694	18.758	45.137	80270	9.06
30	0.9257	2.6181	7.0506	17.352	41.370	79600	8.91
40	0.8772	2.4200	6.5222	15.889	37.478	78763	8.74
50	0.8278	2.2239	5.9931	14.444	33 669	77843	8.55
60	0.9111	2.5219	6.9556	17.389	41.434	80214	9.01
65	0.9951	2.8403	7.9444	20.222	49.134	81865	9.34
70	1.0787	3.1561	8.9167	23.000	56.741	83125	9.6
75	1.1644	3.4792	9.9028	25.856	64.581	84179	9.8
80	1.2486	3.7988	10.8861	28.667	72.391	85054	10.0

mixtures can be represented as a function of temperature T (in °K) by equation (9).

$$\ln k = a' - b'T \qquad \ldots (9)$$

The values of the constants a′ and b′ were evaluated by the method of least squares and are compiled in Table 2, for each solvent composition. The velocity constants calculated from equation (9) at the five temperatures are accurate within the experimental error for the various dioxane-water solvents.

The addition of dioxane to water first causes a decrease of reaction rate, activation energy or frequency factor, to a minimum at about 54% by weight dioxane, which is then followed by an increase on further dioxane addition. However, the effect of solvent on reaction rate is more pronounced on increasing the temperature. This behaviour for the specific reaction rate was recently reported for acetamide[5] and formamide[6] hydrolyses in dioxane-water solvent mixtures. Accordingly, it is possible to correlate the reaction rate with solvent effects in the same manner[5,6]. The decrease in activation energy may be due to more solvation of the activated complex than of the reactants.

Solvation effects and activation parameters :

The influence of solvent variation on reaction rate may be examined in terms of changes in the activation parameters. These parameters are usually taken as a measure of the solvation effects, and can be calculated by applying the usual thermodynamic relations to the temperature variation of the rate constant in various dioxane-water solvents. According to the theory of absolute reaction rates the rate constant is related to the free energy of activation, $\triangle G^*$, by the equation

$$k = \frac{KT}{h} e^{-\Delta G^*/RT}.$$

Thus, $\triangle G^*$ can be represented as a function of temperature by (10).

$$\triangle G^* = RT\left(\ln \frac{KT}{h} - \ln k\right) = R(T \ln T + c\,T + b') \ldots (10)$$

where $c = \ln\frac{K}{h} - a^1$. The value of the constant c for each solvent composition was evaluated, and is given in Table 2. Thus,

$$\triangle S^* = -d(\triangle G^*)/dT = -R(\ln T + 1 + c) \quad \ldots (11)$$

$$\triangle H^* = \triangle G^* + T\triangle S^* = R(b' - T) \quad \ldots (12)$$

TABLE 2 – CONSTANTS OF EQUATIONS (9-12) FOR EVALUATION OF K AT DIFFERENT TEMPERATURES AND THERMODYNAMIC ACTIVATION PARAMETERS AT 25°C, IN DIOXNE-AWATER MIXTURES

Dioxane Wt %	a′	b′	c	25°C $\triangle G^*$ ± 952 J mole^{-1}	$\triangle H^*$ ± 495	$-\triangle S^*$ ± 1.5 J mole^{-1} K^{-1}
0	21.4130	9792.42	2.3469	101360	78939	75.2
5	21.2903	9763.41	2.4696	101423	78698	76.2
10	21.1487	9728.56	2.6112	101484	78408	77.4
20	20.8500	9655.27	2.9100	101615	77799	79.9
30	20.5245	9574.66	3.2355	101752	77129	82.6
40	20.1279	9473.97	3.6321	101898	76291	85.9
50	19.6934	9363.30	4.0665	102055	75371	89.5
60	20.7444	9648.52	3.0155	101821	77743	80.8
65	21.5022	9847.13	2.2578	101594	79394	74.5
70	22.0941	9998.61	1.6658	101386	80654	69.5
75	22.5987	10125.47	1.1612	101190	81708	65.3
80	23.0240	10230.66	0.7360	101010	82583	61.8

The calculated thermodynamic parameters of activation at 25° for various solvent compositions are recorded in Table 2 and are shown in Fig. 1. It is seen that $\triangle G^*$ increases gradually and linearly with successive dioxane addition up to about 54% by weight and then decreases, also linearly, by further progressive addition of the organic solvent. According to the theory of absolute reaction rates, the increase of $\triangle G^*$ is a sign of solvation of the reacting species.

Some useful insight with regard to the changes in the structural aspects of the solvents might be obtained from the changes in enthalpy and entropy, which contain important structural contributions[9]. The enthalpy change decreases gradually with increasing dioxane content up to about 54% by weight, and thereafter increases with progressive addition of dioxane.

It has been pointed out[10] that the stabilisation of the activated complex by the solvent involves restriction of motion of some of the solvent molecules. Solvents

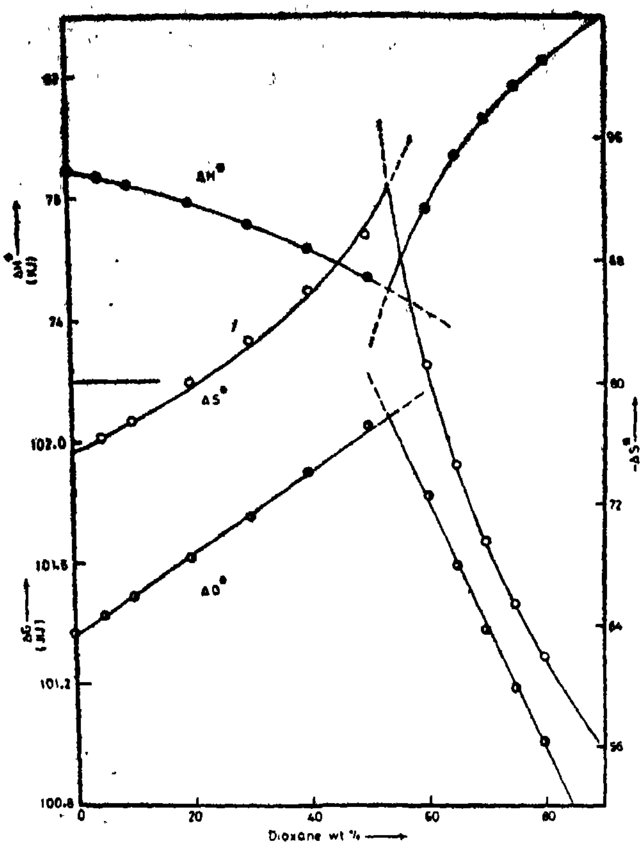


Fig. 1. Variation of activation parameters with solvent composition at 25°

having permanent dipole moments will, therefore, be preferentially oriented such that an attractive interaction rather than repulsion takes place. On the other hand, non-polar solvents will be relatively unoriented and hence will have higher entropy of activation. These solvents will, therefore, have a greater loss in entropy as a result of solvation, and reactions in these solvents will consequently have a large negative entropy of activation.

However, ΔS^*, which has large negative values, decreases with increasing dioxane content up to about 54% by weight, and thereafter increases with further dioxane addition.

The sudden variation of thermodynamic parameters of activation noticed at around 54% by weight of dioxane reflects the variation of reaction kinetics with solvent composition. As mentioned above, minimum rate constant was observed at about 54% by weight of dioxane.

Influence of dielectric constant on reaction rate :

To test equation (6) in a more precise manner, it may be put in the form

$$\log \frac{A}{k} = \frac{E\,b}{2.3026\,R}\,\frac{1}{\log (a/D)}, \text{ or,} \qquad \ldots (13)$$

$$\log \frac{A}{k} \log \frac{a}{D} = \frac{E\,b}{2.3026\,R} = \text{constant.}$$

For any solvent composition, a plot of log (A/k) vs $1/\log (a/D)$ values at different temperatures should yield a straight line, passing through the origin, and of positive slope $(Eb/2.3026\ R)$. From the Arrhenius calculated E values, the b values may be calculated for each solvent composition and compared with the reported[8] b values. Applicability of the developed relation to sixty sets of recently published data on the effects of solvents on the acid and base hydrolyses of amides, anilides and esters (including usual reactions as well as those exhibiting minima or maxima with solvent composition variation) has been examined. Practically, this is the case and the agreement was generally very well. Åkerlof[9] reported that the constant b is a very important factor in the theory for heats of dilution.

Also, from equation (13), a plot of log (A/k) vs $Eb/\log (a/D)$ should yield a straight line passing through the origin for all data in different solvent compositions at different temperatures since the slope is always $1/2.3026\ R$. With more than 600 experimental points, a practically good straight line passing through the origin was obtained and the value of R calculated was 8.3144 J $mole^{-1}K^{-1}$. We must, therefore, expect that any reaction obeying Arrhenius equation should follow equations (6), (8) and (13).

The acid hydrolysis of propionamide has been studied in dioxane-water solvents in different dielectric media in the range 7.85-8.7. Starting from the point of minimum reaction rate (at around 54 wt % dioxane), the rate increases either on increasing (water-rich region) or decreasing (dioxane-rich region) the dielectric constant. At any temperature, log k was found to be linearly dependent on D and gave curves with $1/D$, in both regions.

The influence of dielectric constant on reaction rate, for any solvent composition, may now be best investigated on the basis of our new proposed equations. Equation (13), for example, predicts a linear dependence of log (A/k) on $1/\log (a/D)$ for any solvent composition. Practically good straight lines passing through the origin were generally obtained, and typical plots in the water-rich region (0-50 wt % dioxane) are shown in Fig. 2, for propionamide hydrolysis in dioxane-water solvents. The least square calculated values of log k' are given in Table 3.

Elsemongy[4] deduced equations which relate to the rate constant of a reaction to the dielectric constant of the solution, its ionic strength and temperature. These are applicable to ion-ion, ion-dipole and dipole-dipole reactions. Values of distances of closest approach, $a_{\pm}$ for the activated complex were estimated by substitution in equations[4] for the different values of ln k, ln k' and D at different temperatures. At any tempera-

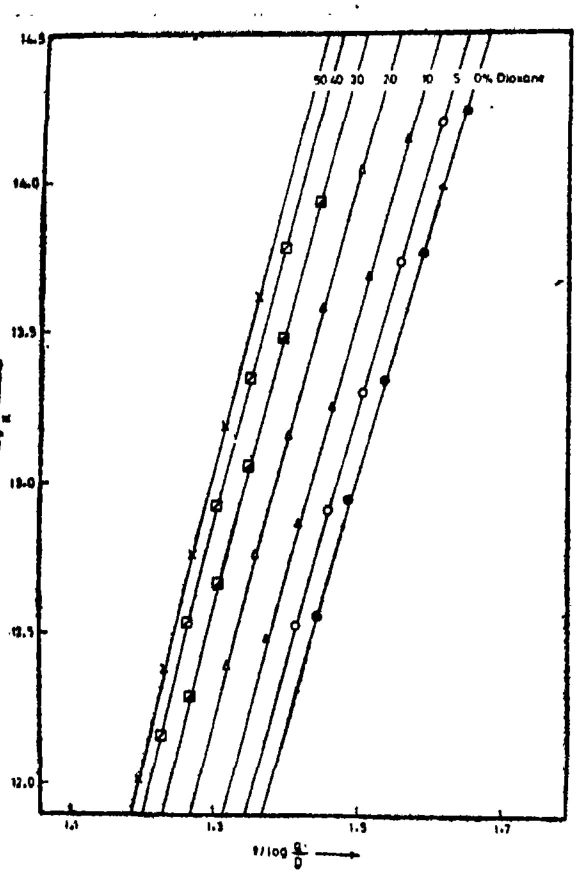


Fig. 2. Influence of dielectric constant on rate constant

TABLE 3—CONSTANTS FOR EVALUATION OF DIELECTRIC CONSTANTS, CALCULATED T°K AT UNIT DIELECTRIC CONSTANT AND LOG K' VALUES FOR VARIOUS SOLVENT COMPOSITIONS

Dioxane Wt %	C_S mole/l	C_{H_2O} mole/l	log a*	b	T°K at which D = 1	log k'
0	0.000	55.51	2.50606	0.00205	1222.5	5.8207
5	0.568	52.73	2.49248	0.00209	1192.6	5.6906
10	1.135	49.96	2.48417	0.00215	1155.5	5.5283
20	2.270	44.41	2.45166	0.00224	1094.5	5.2241
30	3.405	38.86	2.40984	0.00233	1034.3	4.8936
40	4.540	33.31	2.35179	0.00241	975.8	4.5262
50	5.675	27.75	2.27118	0.00247	919.5	4.1326
60	6.810	22.20	2.15484	0.00249	865.4	4.1663
65	7.378	19.43	2.07052	0.00247	838.3	4.2391
70	7.945	16.65	1.97822	0.00245	807.4	4.2151
75	8.513	13.88	1.86669	0.00240	777.8	4.1660
80	9.080	11.10	1.70059	0.00225	755.8	4.1275

* Calculated on the absolute temperature scale

Calculated from the interpolated values

ture $a_{\ddagger}$ varies with solvent composition, i.e., with dielectric constant[4]. In the acid hydrolysis of amides, it was supposed[5-7] that the catalysing ion is unipolar in character ($Z_A = 1$) whereas the amide molecule is a dipole. The dipole moment and radius of the propionamide molecule were taken[11] as equal to 3.85×10^{-18} esu and 3.07×10^{-8} cm, respectively. The radius of the hydronium ion[3-4] was taken as 1.7×10^{-8} cm. The results of our calculations at 25, 45 and 65°, are given in Table 4.

TABLE 4—DISTANCES OF CLOSEST APPROACH, $a_{\ddagger}$, FOR THE ACTIVATED COMPLEX AND DIELECTRIC CONSTANTS AT DIFFERENT TEMPERATURES

Dioxane Wt %	D 25°C	D 35°C	D 45°C	D 55°C	D 65°C	$a_{\ddagger}$ 25°C	$a_{\ddagger}$ 45°C	$a_{\ddagger}$ 65°C
0	78.5	74.9	71.4	68.1	65.0	3.119	3.137	3.154
5	74.0	70.5	67.2	64.1	61.1	3.136	3.155	3.173
10	69.7	66.3	63.1	60.1	57.2	3.158	3.178	3.198
20	60.8	57.7	54.8	52.1	49.5	3.199	3.221	3.243
30	51.9	49.2	46.6	44.2	41.9	3.243	3.268	3.293
40	43.0	40.7	38.5	36.4	34.4	3.293	3.321	3.349
50	34 3	32.4	30.6	28.9	27.3	3.346	3.377	3.407
60	25.8	24.4	23.0	21.8	20.6	3.337	3.370	3.405
65	21.6	20.4	19.3	18.2	17.2	—	—	—
70	17.7	16.7	15.8	14.9	14 1	3.320	3.357	3.394
75	14.2	13.4	12.7	12.0	11.4	—	—	—
80	10.7	10.2	9.7	9.2	8.7	3.296	3.335	3.373

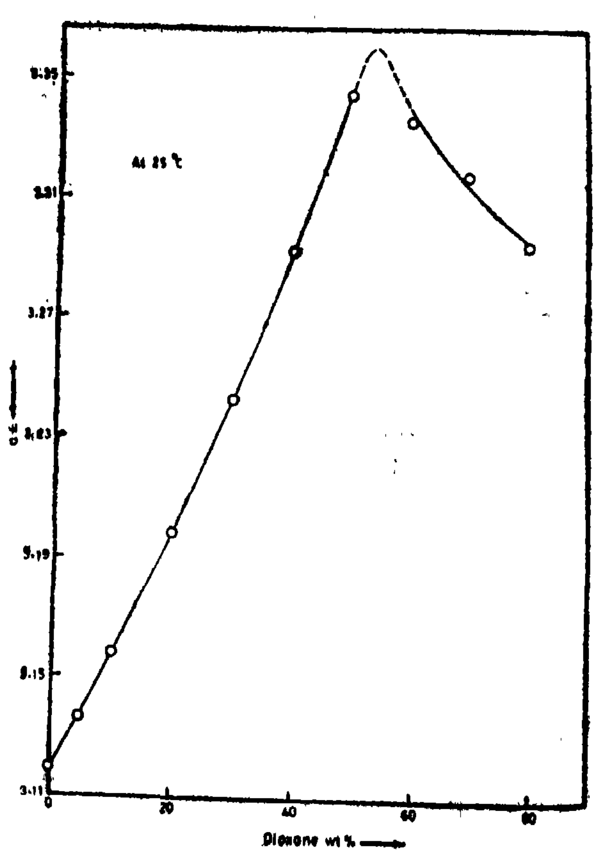


Fig. 3. Dependence of distance of closest approach for the activated complex on solvent composition

At any temperature, the a_+ value increases on successive addition of dioxane, reaches a maximum at around 54% by weight (minimum reaction rate) and thereafter decreases on further dioxane addition (Fig. 3). As the distance of closest approach for the activated complex decreases, the reacting species become closer to each other, and the reaction rate increases. This may explain the variation of reaction rate with solvent composition and may also account for the solvation of the activated complex. According to the Kirkwood theory[1,2] these radii should not correspond to the over-all radii but should be effective radii related to the size of the active groups in the complex molecules. Therefore the essential factor is the closeness of approach of the solvent molecules to the seat of reaction. The distance of C–O bond reported[1] is of the order 1.43 Å. Therefore it is reasonable that the new bond which is being formed in the transition state due to the attack of H_3O^+ ion (its radius was taken[2-4] as 1.7 Å) on the carbonyl oxygen atom of the amide is of the order 1.43 + 1.7 = 3.13 Å. This value is in full agreement with our calculated value of 3.119 Å at 25° in the aqueous medium. On this basis the values calculated are entirely reasonable and give an idea about the extent of solvation.

Thus, the best method for computation of the distance of closest approach of solvent molecules to the transition state is to (1) calculate the value of log k′ using one of our proposed equations (7) or (8), and (2) substitute in equations[4] for the different values of ln k, ln k′ and D at different temperatures.

However, a weakness in Elsemongy's calculations[4] is the assumption of constant radii for reactant particles at all temperatures and all solvent compositions when calculating theoretical activated complex radii from the derived equations[4]. In addition, constant radii for reactant particles were assumed even when the nature of the second component of the solvent changed completely[4]. It would be seen that not only the radius of the intermediate complex, but also the radii of reactant particles should all change with the nature of solvent, with the composition of a given solvent pair, and with the temperature for a given solvent. However, further investigations[12] would be helpful to account for these defects and to throw more light on the influence of solvent on reaction rates and mechanisms.

Proposed mechanism :

A bimolecular mechanism for the acid hydrolysis of acetamide in aqueous-organic mixed solvents was recently reported[8]. Based on the experimental findings, this mechanism was modified in a more general form to account for the influence of the solvent on the acid hydrolysis of propionamide. Our proposed protolytic mechanism may be simply represented as follows :

i) $A + SH^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} T^+ + S$ (fast pre-equilibrium)

ii) $T^+ + H_2O \xrightarrow{k_2}$ products, (slow)

where A is the amide molecule, S is an organic solvent molecule and T^+ stands for the solvated transition state in which the solvation is maintained through H-bonding. One must also consider the equilibrium[8] $H_3O^+ + S \rightleftharpoons SH^+ + H_2O$. For this reaction, the equilibrium constant will be written as

$$K = C_{SH}+ C_{H_2O}/C_{H_3O}+ C_S \qquad \ldots (15)$$

and

$$(C_{H_3O}+)_{total} = C_{H_3O}^+ + C_{SH}^+$$

$$= (C_{SH+}C_{H_2O}/K\ C_S) + C_{SH}^+$$

$$= C_{SH}^+ (1 + C_{H_2O}/K\ C_S) \qquad \ldots (16)$$

Application of the steady-state treatment of the species T^+ and substituting in the rate expression, one gets,

$$\text{the rate} = k_2\ C_T^+ C_{H_2O} = \frac{k_1\ k_2\ C_A\ C_{SH}^+}{k_{-1}\ C_S/C_{H_2O} + k_2} \qquad \ldots (17)$$

Substitution of the value of C_{SH}^+ from equation (16) into equation (17), we obtain

$$\text{the rate} = \frac{k_1\ k_2\ C_A}{k_{-1}\ C_S/C_{H_2O} + k^2}\ \frac{(C_{H_3O}^+)_{total}}{1 + C_{H_2O}/K\ C_S}$$

The observed second-order rate constant is therefore given by

$$k = \frac{k_1\ k_2}{(k_{-1}\ C_S/C_{H_2O} + k_2)(1 + C_{H_2O}/K\ C_S)} \qquad \ldots (18)$$

Equation (18), on arrangement, gives

$$\frac{1}{k} = \left(\frac{1}{k_1} + \frac{k_{-1}}{k_1\ k_2}\ \frac{C_S}{C_{H_2O}}\right) + \left(\frac{k_{-1}}{k_1\ k_2\ K} + \frac{1}{k_1\ K}\ \frac{C_{H_2O}}{C_S}\right) \quad (19)$$

The minimum of a reaction rate indicates a compensation of two opposing factors affecting the reaction rate. It is obvious, from equation (19), that k is dependent on both C_{H_2O}/C_S and C_S/C_{H_2O}. So, this may explain the variation of rate constant with solvent composition. If the reactions were catalysed only by SH^+ ion, the second-order velocity constant would be given, from equation (17) as

$$k_{SH^+} = \frac{k_1\ k_2}{k_{-1}\ C_S/C_{H_2O} + k_2} \qquad \ldots (20)$$

which, on rearrangement, gives

$$\frac{1}{k_{SH^+}}=\frac{1}{k_1}+\frac{k_{-1}}{k_1\ k_2}\ \frac{C_S}{C_{H_2O}} \qquad \text{— (21)}$$

On the other hand, substitution of C_{SH^+} into equation (17) by its value from equation (15) gives the velocity constant of the reaction if it were catalysed only by H_3O^+ ion.

$$k_{H_3O^+}=\frac{k_1\ k_2\ K}{k_{-1}+k_2\ C_{H_2O}/C_S} \qquad \text{... (22)}$$

$$\frac{1}{k_{H_3O^+}}=\frac{k_{-1}}{k_1\ k_2\ K}+\frac{1}{k_1\ K}\ \frac{C_{H_2O}}{C_S} \qquad \text{... (23)}$$

Comparison of equations (21) and (23) with equation (19) leads to equations (24) and (25).

$$\frac{1}{k}=\frac{1}{k_{SH^+}}+\frac{1}{k_{H_3O^+}} \qquad \text{... (24)}$$

$$k=\frac{k_{SH^+}\ k_{H_3O^+}}{k_{SH^+}+k_{H_3O^+}} \qquad \text{... (25)}$$

It is clear, from equations (24) and (25), that if $k_{H_3O^+}$ is much smaller than k_{SH^+} the observed second-order rate constant k will be nearly given by $k_{H_3O^+}$. From equations (20) and (22), we obtain

$$k_{H_3O^+}/k_{SH^+}=K\ C_S/C_{H_2O}=C_{SH^+}/C_{H_3O^+} \qquad \text{... (26)}$$

and thus, from equations (24) and (26),

$$k_{H_3O^+}/k=1+K\ C_S/C_{H_2O} \text{ and } k_{SH^+}/k=1+C_{H_2O}/K\ C_S \qquad \text{... (27)}$$

So, if the value of the equilibrium constant K (equation 15) is known in dioxane-water mixtures, the values of both $k_{H_3O^+}$ and k_{SH^+} may be calculated for any solvent composition.

Now it is obvious, from equation (19), that in the water-rich regions the contribution of the first term in the bracket to the observed rate constant predominates, whereas the contribution of the second term predominates in the dioxane-rich region. Thus, to test the validity of our proposed equations, 1/k was plotted versus C_S/C_{H_2O} and versus C_{H_2O}/C_S in the water-rich (0-50 wt % dioxane) and in the dioxane-rich (60-80 wt % dioxane) regions, respectively. From the initial rate slope and intercept in each region, the k_{-1}/k_2 ratio can be determined and compared to each other. In the former case, from the initial slope of the curve obtained $\left(\frac{1}{k_1}\ \frac{k_{-1}}{k_2}\right)$ and its initial intercept $\left(\frac{1}{k_1}\right)$, the k_{-1}/k_2 ratio equals 2.25 at 25°. In the latter case, practically linear plot was obtained at the same temperature ; from its slope $\left(\frac{1}{k_1\ K}\right)$ and intercept $\left(\frac{k_{-1}}{k_2}\ \frac{1}{k_1\ K}\right)$, the k_{-1}/k_2 ratio was found to be 4.27. Thus, the k_{-1}/k_2 ratio varies from 2.25 to 4.7 on passing from water-rich to dioxane-rich regions. The linear dependence of 1/k on C_{H_2O}/C_S in the dioxane-rich region shows that the contribution of the first term in equation (19) is mainly negligible, and that the k_{-1}/k_2 ratio (or k_2) is almost constant in this region.

The values of the Arrhenius parameters for the acid hydrolysis of propionamide in dioxane-water solvents together with the thermodynamic activation parameters are all consistent with the above considerations and confirm our proposed mechanism for the reaction.

Acknowledgement

The authors express their thanks to Mrs. Laila Abu Elela for her encouragement, guidance and helpful criticism.

References

1. LALLAN SINGH, R. T. SINGH R. K. SINGH and R. C. JHA, *J. Indian Chem. Soc.*, 1978, 55, 372.
2. K. J. LAIDLER and P. A. LANDSKROENER, *Trans. Faraday Soc.*, 1956, 52, 200.
3. E. S. AMIS and J. F. HINTON, Solvent Effects on Chemical Phenomena, Vol. I, Academic Press, New York, London, 1973.
4. M. M. ELSEMONGY, *Z. Physik Chem. Neue Folge*, 1973, 84, 294.
5. M. M. ELSEMONGY, M. S. ABU ELAMAYEM and M. MOUSSA, *Z. Physik. Chem. Neue Folge*, 1975, 95, 215.
6. M. M. ELSEMONGY and H. M. ABU ELNADER, *J. Indian Chem. Soc.*, 1977, 54, 1055.
7. M. M. ELSEMONGY, M. S. ABU ELAMAYEM, M. MOUSSA and M. GOUDA, *J. Indian Chem. Soc.*, 1975, 52, 1130.
8. G. ÅKERLOF and O. A. SHORT, *J. Amer. Chem. Soc.*, 1936, 58, 1241.
9. G. ÅKERLOF, *J. Amer. Chem. Soc.*, 1932, 54, 4125.
10. K. B. WIBERG, Physical Organic Chemistry, John Wiley, New York, 1963.
11. M. E. HOBBS and W. W. BATES, *J. Amer. Chem. Soc.*, 1952, 74, 746.
12. To be published.

J. Indian Chem. Soc.,
Vol. LVII, May 1980, pp. 513-516

Reaction Between an Ethanolic Solution Containing the Anion $[Rh(CO)_2Cl_2]^-$ and Gaseous Sulphur Dioxide

G. N. SALAITA, F. H. JUMEAN and M. N. MULKI

Department of Chemistry, Faculty of Science, University of Jordan, Amman, Jordan

Manuscript received 8 December 1978, revised 30 July 1979, accepted 31 December 1979

The kinetics of the reaction between $[Rh(CO)_2Cl_2]^-$ and SO_2 was followed spectrophotometrically at 390 nm and a temperature study to determine activation parameters was carried out. The observed rate constants were calculated from the initial slopes and the reaction was found to be first order with respect to each of the reactants. Infrared spectral data suggest the presence of Rh-S and S-C bonds in the product and a shift in one of the CO bands was observed. These observations, in conjunction with the high negative entropy of activation (−64.6eu), suggest that SO_2 is inserted between Rh and CO. The data were found to obey a rate equation analogous to the Michaelis-Menten equation employed in the analysis of enzyme kinetic data.

THE complex ion $[Rh[CO)_2Cl_2]^-$ is prepared by refluxing an ethanolic solution of rhodium trichloride with carbon monoxide giving a yellow coloured solution[1]. When sulphur dioxide is subsequently passed through this solution, the colour changes to orange. Infrared evidence obtained in this work suggest that SO_2 is inserted between the metal and CO. It is of interest to note that if the orange solution is concentrated the resulting solid is the dark red complex[1] $[Rh(SO_2)Cl(H_2O)_2]$. Infrared measurements[1] confirm the absence of CO in this solid complex.

In recent years a great deal of interest has been given to insertion reactions involving transition metal complexes. Insertion reactions occur frequently in the general area of catalysis, particularly in the reversible oxygenation of metal complexes involving synthetic oxygen carrying systems. These studies initially dealt with group VIII square planar complexes with particular emphasis on the type and degree of the metal-ligand bond. Later, however, they were broadened to include carbon monoxide, sulphur dioxide and ethylene metal complexes.*

Attention was heretofore focused on synthetic aspects and few kinetic studies were undertaken[2]. This has been true in the case of sulphur dioxide insertion reactions as well. Following the discovery of these insertion reactions[3] attention has been entirely focused on synthetic aspects[4] and it was not until recently[5,6] that kinetic considerations were attended to.

This paper deals with the kinetics and mechanism of the reaction between sulphur dioxide and $[Rh(CO)_2Cl_2]^-$ in absolute ethanol.

* Reference 1 and references cited therein.

Experimental

Materials : All chemicals used were of reagent grade unless otherwise specified. Rhodium trichloride was purchased from Johnson Matthey Chemicals Ltd., London. Liquified sulphur dioxide was purchased from BDH Chemicals Ltd., London. Carbon monoxide was generated by reacting formic acid with sulphuric acid.

Preliminary procedure : The complex ion $[Rh(CO)_2Cl_2]^-$ was prepared[10] by passing carbon monoxide through an ethanolic solution of rhodium trichloride (0.20 g in 30ml ethanol). The solution was refluxed for five hours with continuous stirring. During this time the color of the solution slowly changed from dark red to pale yellow. The infrared spectrum of the resulting solution indicated the presence of CO stretching bands at 2010 and 2080 cm^{-1}.

The concentrations of sulphur dioxide in ethanolic solutions were determined by iodometry.

Kinetics : The reaction between sulphur dioxide and $[Rh(CO)_2Cl_2]^-$ was followed at 390 nm on a unicam SP 8000 spectrophotometer in the temperature range, $15-30\pm0.5°$. The reagent solutions were thermostated seperately for at least 20 min. before the reaction was initiated by rapid mixing.

The order of the reaction with respect of sulphur dioxide and $[Rh(CO)_2Cl_2]^-$ was determined from the initial rates by varying the concentration of one species while holding the other constant. The rate constants were calculated from the initial rates.

Infrared measurments were carried out on ethanolic solutions containing the insertion complex using a Perkin Elmer 257 grating spectrophotometer.

Results

1. *Kinetic Measurements* : Plots of initial rate of change of absorbance for various solutions containing equimolar concentrations of $[Rh(CO)_2Cl_2]^-$ $(6.0\times10^{-4}M)$ and varying concentrations of sulphur dioxide $(0.024-1.162M)$ were found to be linear and passing through the origins. The reference path had two cells in tandem, one containing sulphur dioxide and the other the complex ion. The sample path also had two cells in tandem, one cell containing the complex ion and sulphur dioxide, both of the same initial concentration as in the reference path, and the other cell containing pure solvent. Thus, at the time of initiation of the reaction the absorbance reading was zero.

TABLE 1 (a)—DEPENDENCE OF THE OBSERVED RATE CONSTANT, k_{obs}, ON (SO_2). $[Rh(CO)_2Cl_2]^-=6.0\times10^{-4}M$. SOLVENT : ETHANOL. TEMP. $=25\pm0.5$°C.

(SO_2) M	$k_{obs}\times10^3$ min^{-1}
0.024	1.30
0.032	2.00
0.042	2.32
0.092	4.35
0.120	5.80
0.475	14.27
1.162	20.60

The dependence of the observed rate constant, k_{obs}, on the concentration of sulphur dioxide is given in Table 1 (a).

The order of the reaction with respect to the complex ion was determined by varying the concentration of the complex ion in the range $(1.8-27)\times10^{-4}M$ with a fixed sulphur dioxide concentration of $0.03M$.

TABLE 1 (b)—DEPENDENCE OF THE OBSERVED RATE CONSTANT k_{obs} ON THE CONCENTRATION OF $[Rh(CO)_2Cl_2]^-$. $(SO_2)=0.03M$. SOLVENT : ETHANOL. TEMP. $=25\pm0.5$°C.

$[Rh(CO)_2Cl_2]^-\times10^4$ M	$k_{obs}\times10^3$min^{-1}
1.8	0.94
6.0	1.90
9.0	3.00
12.0	3.60
27.0	5.20

From Table 1(b) it is clear that the order with respect to the complex ion is unity.

A plot of k_{obs} against sulphur dioxide concentration is shown in Fig. 1. It is evident from this figure that the reaction is first order with respect to sulphur dioxide at low SO_2 concentrations and zero order at high concentrations.

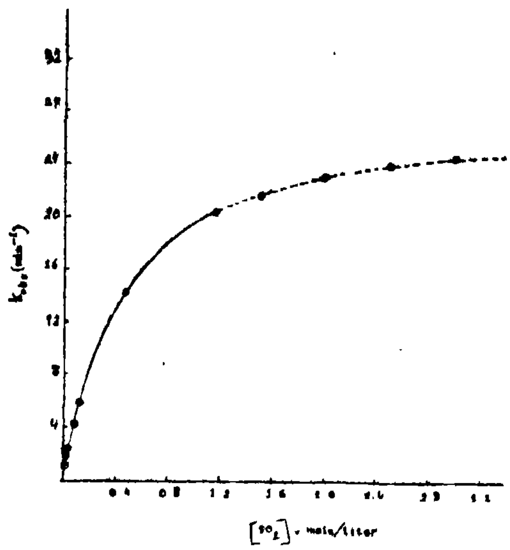


Fig. 1

The dependence of k_{obs} on sulphur dioxide concentration is in agreement with the following rate expression :

$$k_{obs}=\frac{k_1k_2\,(SO_2)}{k_{-1}+k_2(SO_2)} \quad \ldots (1)$$

where k_1 and k_{-1} are the rate constants for the forward and reverse steps, respectively, in the process leading to the formation of the activated species, and k_2 is the rate for the decomposition of the activated species. k_{-2} does not appear in the above rate expression because the reaction essentially proceeds to completion.

Equation (1) may be rearranged as follows :

$$\frac{1}{k_{obs}}=\frac{K_{-1}}{k_1k_2}\;\frac{1}{(SO)_2}+\frac{1}{k_1} \quad \ldots (2)$$

Fig. 2 is a plot of $\frac{1}{k_{obs}}$ against the reciprocal of the sulphur dioxide concentration. The linearity of this plot confirms the validity of the rate expression as given in equations (1) and (2). k_1, as obtained from the intercept of Fig. 2 has the value of 28.5×10^{-3} min^{-1} and the factor $\frac{k_{-1}}{k_1k_2}$ as obtained from the slope has the value 16.86 min^{-1}. Thus $\frac{k_{-1}}{k_2}=0.48$ and equation (1)

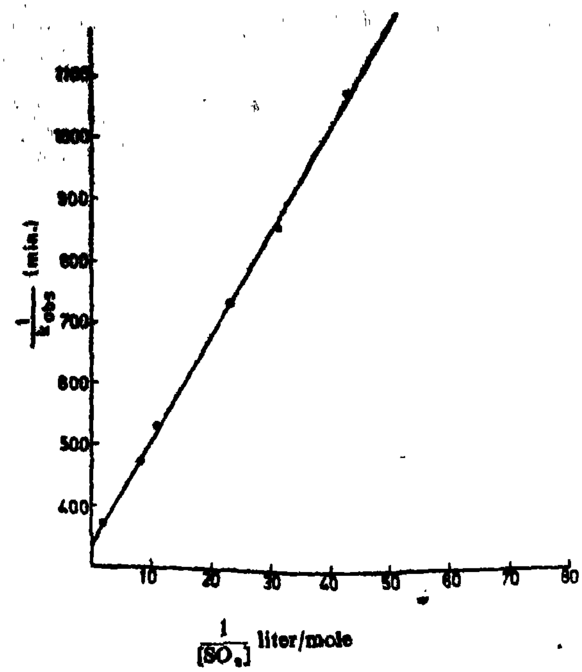


Fig. 2.

becomes :

$$k_{obs} = \frac{28.5 \times 10^{-3}\,(SO_2)}{0.48 + (SO_2)} \quad \cdots (3)$$

The observed initial rate constant for any initial sulphur dioxide concentration can be calculated from this equation as is shown in Table 2.

It is evident that the agreement between the observed and calculated values is quite satisfactory.

TABLE 2—OBSERVED AND CALCULATED RATE CONSTANTS FOR THE REACTION BETWEEN SULPHUR DIOXIDE AND $[Rh(CO)_2Cl_2]^-$. $[Rh(CO)_2Cl_2]^- = 6.0 \times 10^{-4}\,M$.

SO_2 (M)	$k_{obs} \times 10^3$(min^{-1})	$k_{calcd} \times 10^3$(min^{-1})
0.024	1.30	1.37
0.032	2.00	1.80
0.042	2.32	2.29
0.090	4.35	4.00
0.120	5.80	5.70
0.475	14.27	14.16
1.162	20.60	20.27

A temperature study was carried out in order to determine the activation parameters. Table 3 gives the value for k_{obs} at different temperatures. The activation parameters were obtained from a plot of ln $\frac{k}{T}$ against $\frac{1}{T}$ in accordance with Eyring's absolute rate equation ΔS^* was found to be −64.6 e.u. and ΔH^* was found to be 5·8 kcal/mole.

TABLE 3—THE OBSERVED RATE CONSTANTS FOR THE REACTION SO_2 AND $[Rh(CO)_2Cl_2]^-$ BETWEEN= $6.0 \times 10^{-4}\,M$.

T° (k)	$k_{obs} \times 10^3$ min^{-1}
288.5	2.20
293.5	2.70
298.5	3.30
303.5	3.96

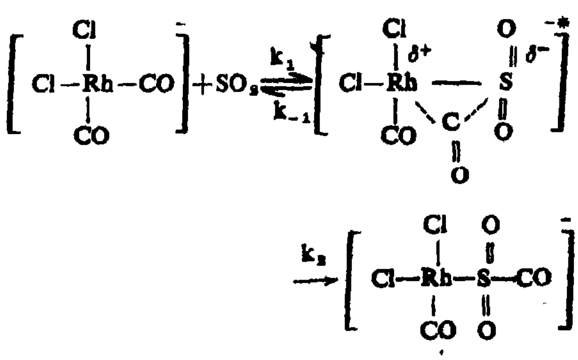
Infrared data on ethanolic solutions of the insertion complex are given in Table 4, together with literature data on $[Rh(CO)_2Cl_2]^-$ and $[Rh(SO_2)\,Cl(H_2O)_2]$ for comparison.

TABLE 4—INFRARED DATA ON $[Rh(CO)_2Cl_2]^-$, $[Rh(SO_2)_2Cl(H_2O)_2]$ AND $[Rh(CO)_2SO_2Cl_2]^-$, IN UNITS OF CM^{-1}.

Compd.	ν(CO)	ν(SO_2)	ν(Rh S)	ν(CS)	Ref.
$[Rh(CO)_2Cl_2]^-$	2010,1080	none	none	none	1
$[Rh(SO_2)_2Cl(H_2O)_2]$	none	1150,1070 910,525		none	1
$[Rh(CO)_2SO_2Cl_2]$	1975,2050	1070,910 530	1150	700, 1610	This work

Discussion

The following mechanism for the reaction between $[Rh(CO)_2Cl_2]^-$ and sulphur dioxide is proposed on the basis of the kinetic and infrared evidence.

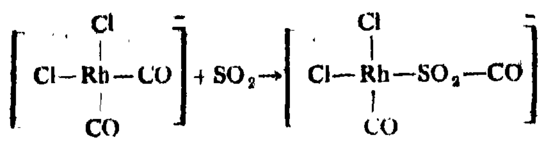


The structure of the activated complex is proposed on the basis of the large negative value of the entropy of activation. Such a large value is normally associated with a charged intermediate or a geometrically restricted

complex. It is probable that both of these factors are significant in this case although the precise contribution of each to $\triangle S^{*}$ cannot be ascertained. Sulphur dioxide is highly solvated in ethanol[8] and the loss of the solvation shield upon binding to the complex ion is thus expected to increase the entropy of activation.

Further evidence for the proposed mechanism is furnished by infrared measurements carried out on the complex in solution (Table 4). The presence of S-C and Rh-S bonds in the product indicates the formation of an insertion product. The appearance of infrared bands at 700 cm^{-1} and 1610 cm^{-1} indicates the formation of an S–C bond, whereas the presence of a band at 1150 cm^{-1} strongly suggests the formation of an Rh-S bond. Furthermore, the presence of three broad bands at 1071 cm^{-1}, 910 cm^{-1} and 530 cm^{-1} is a strong indication for the appearance of SO_2[1,7].

The one-step mechanism



which is consistent with a very short-lived intermediate ($\tau = 10^{-13}$ sec or less), may be excluded on the basis of experimental evidence from the literature and from this work. For example, Martin *et al*[9], point out that such a single insertion step is normally associated with free radical reactions, a situation that clearly does not arise in this work. Secondly, the observation that the reaction rate does not continue to increase indefinitely as the ligand concentration is raised (Fig. 1) indicates that the mechanism is more complex than a simple bimolecular collision. The finding that the data could be fitted to equation 3 (as evidenced by Fig. 2), also serves to illustrate this point.

In addition to the above evidence, application of the continuous variation method to the reaction showed that the ratio[11] of complex to sulphur dioxide in the product is 1 : 1 (to be published). It is noteworthy that a further but extremely slow reaction takes place following the insertion of sulphur dioxide. In this reaction another sulphur dioxide molecule, as evidenced by the continuous variation method, reacts with the product to form a new complex[11] in which the ratio of complex to sulphur dioxide is 1 : 2.

Despite the large negative entropy of activation the reaction proceeds at a moderate rate because of the low $\triangle H^{*}$ value (5.8 Kcal/mole).

Analogy with Enzyme Kinetics : It may be noted that the present reaction is analogous to enzymatic reactions. In both cases an activated complex is formed from the reactants in a reversible process with rapid forward and back rates. This is followed by a slow step involving the breakdown of the activated complex into products.

Thus, the observed rate constant in enzymatic reactions as given by the Briggs and Haldane equation (4) is expected to behave in a similar way to k_{obs} in our reaction, upon varying the substrate concentration [analogous to (SO_2)].

In the equation,

$$k_{obs} = \frac{k_2}{1 + \frac{k_m}{(S)}} \quad \ldots (4)$$

the Michaelis constant is given by $k_m = \frac{k_{-1} + k_2}{k_1}$ and (S) is the substrate concentration. It is easily seen that substitution of $\frac{k_{-1} + k_2}{k_1}$ for k_m in equation(4) would yield a form identical to equation (1), in which SO_2 plays a similar role to the substrate S, at a fixed enzyme and complex ion concentrations, respectively.

Acknowledgement

The authors are grateful to Dr. E. C. Watton, UNESCO Professor at the University of Jordan, for his suggestions and comments during this work.

References

1. M. K. Fayyad, Dissertation, University of Jordan, 1974.
2. J. E. Stephen and W. Andrew, *J. Amer. Chem. Soc.*, 1973, 95, 6962.
3. J. P. Bilfrt and A. Wojcicki, *J. Amer. Chem. Soc.*, 1974, 96, 5052.
4. S. E. Jacobson, P. Rsohroswig and A. Wojcicki, *Inorg. Chem.*, 1973, 12, 717.
5. J. J. Alexander and A. Wojcicki, *Inorg. Chem. Acta*, 1971, 5, 655
6. G. M. Whitesides and D. J. Boschetto, *J. Amer. Chem. Soc.*, 1971, 93, 1529
7. L. J. Bellamy, The Infrared Spectra of Complex Molecules, Second Edition, Wiley, New York, 1966, p. 355.
8. S. E. Jacobson and A. Wojcicki, *J. Chem. Soc.*, 1973, 95, No. 21, 6962.
9. T.W. Martin, R. E. Rummel and R. C. Cross, *J. Amer. Chem. Soc.*, 1964, 86, 2595.
10. J. Chatt, B. L. Shaw and A. F. Field, *J. Chem. Soc.*, 1966, A, 78.
11. G. N. Salaita, F. H. Jumean and M. N. Mulki, *Inorg. Chem. Acta*,, 1978, 26, 221.

J. Indian Chem. Soc.,
Vol. LVII, May 1980, pp. 517-520

Solid State Kinetics from Thermogravimetry for Diodoquin Complexes of Barium, Magnesium and Cadmium

ALKA MITTAL, A. D. KELKAR* and G. V. GHOLAP

Department of Chemistry, Holkar Science College, Indore-452 001 (M. P.)

Manuscript received 3 August 1979, accepted 9 February 1980

Kinetic parameters, such as order of reaction, energy of activation and frequency factor are determined for the thermal decomposition of the complexes of Ba, Mg and Cd with 5, 7 Diiodo-8-hydroxyquinoline (Diodoquin) (DIHQ). The methods applied are Freeman-Carroll, Coats and Redfern and Horowitz and Metzger.

For the thermal decomposition of DIHQ, complexes of Ba, Mg and Cd, the n and E values are 0, ~1 and 1 and 27.45, 18.06 and 18.72 Kcals/mole by Freeman-Carroll method. The E and Z values by Coats and Redfern method are 28.76, 17.56 and 18.53 Kcals/mole and 2.6×10^{5}, 1.699×10^{4} and 2.113×10^{4} sec^{-1}, while the values of E and Z by Horowitz and Metzger method are 29.169, 17.603 and 18.453 Kcals/mole and 2.28×10^{5}, 1.58×10^{4} and 2.00×10^{4} sec^{-1} respectively.

SURVEY of literature shows that the thermal decomposition of the Ba, Mg and Cd complexes of halogenated oxines are not studied. However, mention can be made of some attempts in this field in which the complexes of these metals with somewhat related ligands were studied.

For barium attempt of Thomas[1], for magnesium attempts of Dupuis[2], Borrel and Paris[3] and for cadmium attempts of Berg[4] and Majumdar[5] are some of the important contributions. But these workers too, have not determined the kinetic parameters and hence this work is undertaken in the present paper. Kinetic parameters like the order of reaction, n, the activation energy, E and the frequency factor, Z are determined by the application of Freeman-Carroll method[6], Coats and Redfern method[7] and Horowitz-Metzger method[8].

Experimental

Thermogravimetry :

Thermograms were taken with a Stanton self recording thermobalance of 1 mg sensitivity using 100 m gms of the sample in a platinum crucible. The heating rate was maintained to be constant at 6° per minute.

The details of preparation of the complex and the metal estimation in each is given in our earlier publication[9]. The complexes were prepared in 1:2 (M:L) ratio and it was confirmed by estimation of elements.

In Freeman-Carroll method the values of dW/dT are obtained from the temperature vs weight loss curves, while in Horowitz-Metzger method T_s is taken as the reference temperature at which dW/dT is maximum.

Results and Discussion

Figure 1 represents a plot in weight loss vs temperature as read from the therm grams. The curve A is for Ba-DIHQ complex, curve B for Mg-DIHQ complex and curve C for Cd-DIHQ complex. The

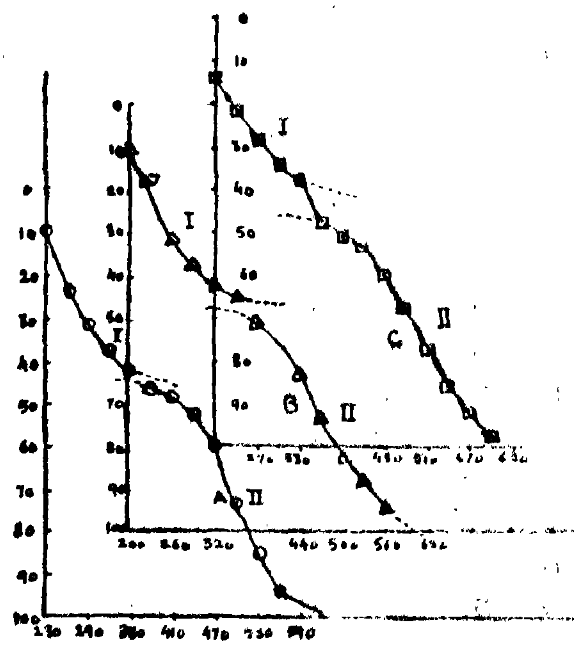


Fig. 1. Curve A—For Ba-DIHQ Complex.
Curve B—For Mg-DIHQ Complex
Curve C—For Cd-DIHQ Complex

I—First step
II—Second step
X-axis—Temp. °C
Y-axis—Weight loss in mgms.

decompositions of DIHQ complexes of Ba, Mg and Cd starts at 230°, 200° and 210° respectively. All these curves are quite steep in the beginning representing faster reactions and thus if the process as a whole is considered as one step, reliable results are not obtained. Thus the whole process of decomposition, in case of each complex, is regarded to be taking place in two steps as shown in the figure. I steps upto 350°, 350° and 330° and II steps above these temperatures for the respective complexes. Since in all these cases the II steps are complete, therefore they are taken into account for obtaining the results. The difference in final weight loss of the II steps and the weight loss at the beginning of the step is regarded as the final weight loss and the weight losses at the starting temperatures of these steps are treated as zero. Accordingly the results are recorded in the Table 1 (for Ba-DIHQ), Table 2 (for Mg-DIHQ) and Table 3 (for Cd-DIHQ) for all the three methods.

The curves A, B and C do not show any horizontal portions indicating that no stable intermediate compound is formed. But weight loss ceases near about 560° in case of Ba-DIHQ complex and this might be due to the formation of $BaCO_3$ in accordance with Thomas[10]. Similarly the formation of oxides of Mg and Cd above 570° and above 600° respectively, are indicated which is also in agreement with Thomas[11] for magnesium.

If the weight loss at any particular temperature (380°C) is observed in these cases, then it appears that they follow the order Mg > Cd > Ba, indicating that they should have the order of their stability as Ba > Cd > Mg. This order is in accordance with the natural order of stability given by Irving-Williams[12]. This order is also supported by the entropy values[13] of Ba, Cd and Mg. The same conclusion can be drawn at some higher temperature (440°C).

TABLE 1—BARIUM COMPLEX OF DIODOQUIN (DIHQ)

S. No.	Temp. °K	Wr	Freeman-Carroll method $\frac{\Delta \frac{1}{T} \times 10^3}{\Delta \log Wr}$	$\frac{\Delta \log \frac{dW}{dT}}{\Delta \log Wr}$	α	Coats-Redfern method $\frac{1}{T} \times 10^3$	$\left[\frac{-\log -\ln(1-\alpha)}{T^2}\right]_\theta$	Horowitz-Metzger method T_s is 803°K θ	ln ln $\frac{W_0}{W}$
1	653	51.0	—	—	0.0097	1.5313	7.6341	−150	−4.6159
2	663	50.5	5.3721	−40.93	0.01942	1.508	7.3516	−140	−3.9462
3	673	50.0	5.2093	−29.07	0.0291	1.4858	7.1865	−130	−3.5250
4	683	49.0	2.4660	−11.00	0.0485	1.4641	6.9721	−120	−3.0013
5	693	47.5	1.5630	−10.83	0.0777	1.4430	6.7727	−110	−2.5887
6	703	46.5	2.2391	0.0	0.0971	1.4224	6.6842	−100	−2.2878
7	713	45.0	1.3916	− 7.63	0.1262	1.4025	6.5762	− 90	−2.005
8	723	42.5	0.7823	− 3.52	0.1748	1.3831	6.4355	− 80	−1.6489
9	733	39.5	0.5943	− 2.28	0.2330	1.3642	6.3065	− 70	−1.3272
10	743	37.0	0.6479	− 3.18	0.2816	1.3458	6.2222	− 60	−1.1061
11	753	33.0	0.3582	− 1.5	0.3592	1.328	6.1050	− 50	−0.8088
12	763	28.5	0.2732	− 1.0	0.4466	1.3106	5.9927	− 40	−0.5258
13	773	24.0	0.2279	− 0.744	0.5340	1.2936	5.8935	− 30	−0.2697
14	783	19.5	0.1829	− 0.37	0.6214	1.2771	5.8002	− 20	−0.029
15	793	15.0	0.1413	− 0.139	0.7087	1.261	5.7074	− 10	+0.2102
16	803	12.0	0.1651	− 0.157	0.7670	1.245	5.646	+ 0	+0.376
17	813	8.0	0.0852	+ 0.2686	0.8447	1.23	5.5499	+ 10	+0.6216
18	823	5.5	0.0922	0.0	0.8932	1.215	5.481	+ 20	+0.8054
19	833	3.0	0.0555	+ 0.433	0.9417	1.20	5.3875	+ 30	+1.0453

TABLE 2—MAGNESIUM COMPLEX OF DIODOQUIN (DIHQ)

S. No.	Temp. °K	Wr	Freeman-Carroll method: $\frac{\Delta \frac{1}{T} \times 10^3}{\Delta \log Wr}$	Freeman-Carroll method: $\frac{\Delta \log \frac{dW}{dT}}{\Delta \log Wr}$	α	Coats-Redfern method: $\frac{1}{T} \times 10^3$	Coats-Redfern method: $-\log \left[\frac{-\ln(1-\alpha)}{T^2}\right]_\theta$	Horowitz-Metzger method (T_s is 773°K): θ	Horowitz-Metzger method: $\ln \ln \frac{W_0}{W}$
1	653	49.0	—	—	0.0666	1.5313	6.7918	−120	−2.6795
2	673	46.0	1.6606	−19.854	0.1238	1.4858	6.5349	−100	−2.0262
3	693	42.5	1.2442	−4.5058	0.1905	1.443	6.3563	− 80	−1.5568
4	713	37.0	0.6727	−1.8903	0.2952	1.4025	6.1620	− 60	−1.0506
5	733	30.5	0.4565	−1.0763	0.419	1.3642	5.9952	− 40	−0.6112
6	753	23.5	0.3198	−0.4514	0.5524	1.328	5.8484	− 20	−0.2183
7	773	17.0	0.2449	−0.167	0.6762	1.2936	5.7244	0	+0.1197
8	793	12.5	0.2442	0.0	0.7619	1.261	5.6418	+ 20	+0.3611
9	813	8.5	0.1851	+0.1403	0.8381	1.23	5.5599	+ 40	+0.5995
10	833	5.0	0.1285	+0.4735	0.9048	1.2004	5.4698	+ 60	+0.8556
11	853	22.0	0.0706	+0.4824	0.9619	1.1723	5.3476	+ 80	+1.1844

TABLE 3—CADMIUM COMPLEX OF DIODOQUIN (DIHQ)

S. No.	Temp. °K	Wr	Freeman-Carroll method: $\frac{\Delta \frac{1}{T} \times 10^3}{\Delta \log Wr}$	Freeman-Carroll method: $\frac{\Delta \log \frac{dW}{dT}}{\Delta \log Wr}$	α	Coats-Redfern method: $\frac{1}{T} \times 10^3$	Coats-Redfern method: $-\log \left[\frac{-\ln(1-\alpha)}{T^2}\right]_\theta$	Horowitz-Metzger method (T_s is 773°K): θ	Horowitz-Metzger method: $\ln \ln \frac{W_0}{W}$
1	633	52.0	—	—	0.0095	1.5797	7.6174	−140	−4.6880
2	653	50.0	2.8412	− 5.700	0.0476	1.5314	6.9412	−120	−3.0202
3	673	49.5	10.364	−18.159	0.0571	1.4858	6.8872	−100	−2.8354
4	693	46.5	1.5793	− 5.533	0.1143	1.4430	6.5966	− 80	−2.1116
5	713	42.5	1.0358	− 3.358	0.1905	1.4025	6 3811	− 60	−1.5561
6	733	37.5	0.7040	− 1.5777	0.2857	1.3642	6.2033	− 40	−1.0895
7	753	32.0	0.5254	− 1.0348	0.3905	1 3280	6.0589	− 20	−0.7031
8	773	25.0	0.3209	− 0.1213	0.5238	1.2936	5.9061	0	−0.2985
9	793	19.5	0.8021	0.0	0.6286	1.261	5.8028	+ 20	−0.0097
10	813	14.0	0.2154	+ 0.1828	0.7333	1.23	5.699	+ 40	+0.2791
11	833	10.0	0.2026	+ 0.1923	0.8095	1.2004	5.6217	+ 60	+0.5057
12	853	6.0	0.1267	+ 0.4369	0.8857	1.1773	5.5256	+ 80	+0.7745
13	873	2.0	0.564	+ 0.6347	0.9619	1.1454	5.3678	+100	+1.1844

—9

Kinetics from Thermograms :

The weight losses are read from the weight loss temperature curves at a temperature interval of 10° in case of Ba-DIHQ and at an interval of 20° in cases of Mg-DIHQ and Cd-DIHQ.

Fairly good straight line plots are obtained for all the three methods applied to all the metals.

In the applicability of Freeman-Carroll method some abnormal points are avoided to get a clear picture about most of the points. Similarly in Coats and Redfern method and Horowitz-Metzger method, the straight line plots have either some points in the beginning or some at the end which did not fall on the straight line. This is expected since the decomposition of solids is known not to obey, first order kinetics perfectly, which is as per the observation of Jacobs and Tompkins[14] and Coats and Redfern[15].

The decomposition of the DIHQ complexes of Ba, Mg and Cd have the subsequent values of the order of reaction as zero, nearly one and one. The values of E obtained for Ba-DIHQ complex are 27.456, 28.763 and 29.169 Kcals/mole by the three methods respectively, while for Mg-DIHQ the values are 18.06, 17.563 and 17.603 Kcals/mole and for Cd-DIHQ the values are 18.72, 18.537 and 18.453 Kcals/mole. It clearly shows that the values of E obtained by the three methods for each complex are in perfect agreement. Similarly the values of Z calculated by the latter two methods for Ba-DIHQ are 2.6×10^{5} and 2.285×10^{5} sec^{-1}, for Mg-DIHQ the values are 1.699×10^{2} and 1.586×10^{2} sec^{-1}, while for Cd-DIHQ the values are 2.113×10^{2} and 2.005×10^{2} sec^{-1}. These values of Z by both the methods and for each complex perfectly agree with each other.

Thus the order of E values of Ba, Mg and Cd is Ba>Cd>Mg, which is exactly the same as said before and is also interpretable on the basis of their entropy values, but on the basis of electropositive character the order predicted is Ba>Mg>Cd, which is not perfectly in agreement.

Looking to the abnormally low values of Z, it is concluded that the reactions of decompositions of DIHQ complexes of Ba, Mg and Cd can be classed as "Slow" reactions' and any other probable reason cannot be given.

Acknowledgement

The authors are thankful to the authorities of Chemistry and Analytical Divisions of B.A.R.C., Bombay for their kind help and suggestions and one of the authors (AM) is thankful to the University of Indore, Indore, for the research fellowship and to the college authorities to provide facilities to work.

References

1. G. Thomas, Thesis, Lyon, 1960.
2. T. Dupuis, Thesis, Paris, 1954.
3. M. Borrel and R. Paris, *Anal. Chim. Acta*, 1950, 4, 267.
4. R. Berg, *Z. Anal. Chem.*, 1927, 71, 321.
5. A. K. Majumdar, *J. Indian Chem. Soc.*, 1945, 22, 309.
6. E. Freeman and B. Carroll, *J. Phys. Chem., Ithaca*, 1958, 62, 394.
7. A. W. Coats and J. P. Redfern, *Nature*, 1964, 208, 68.
8. H. H. Horowitz and G. Metzger, *Anal. Chim.*, 1963, 35, 1464.
9. Alka Mittal, A. D. Kelkar and G. V. Gholap, *Chem. and Petro. Chem. Jour.*, 1978, IX 10, 29.
10. G. Thomas, Thesis, Lyon, 1960.
11. G. Thomas, Thesis, Lyon, 1960.
12. H. Irving and R. J. P. Williams, *Nature*, 1948, 162, 746 ; *J. Chem. Soc.*, 1953, 3192.
13. C.N.R. Rao, "A Hand Book of Chemistry and Physics". (Ed.) Affiliated East-West Press Ltd., New Delhi, 1967, p. 172.
14. P. W. M. Jacobs and F. C. Tompkins, "Chemistry of the solid state". Ed. W. E. Garner (Butterworth Scientific Publication, London, 1955, p. 188.
15. A. W. Coats and J. P. Redfern, *J. Polymer Sc.*, 1965, part 3(b), 917.

J. Indian Chem. Soc.,
Vol. LVII, May 1980, pp. 521-523

Polarographic Study of Zn(II)-Acetylacetonate System vis-a-vis the Kinetics of the Electrode Reaction

(Km.) KRISHNA, S. K. JHA and MUKHTAR SINGH

Chemistry Department, Agra College, Agra-282 002

Manuscript received 14 June 1979, revised 13 December 1979, accepted 18 March 1980

Polarographic behaviour of Zn(II) has been studied in the presence of increasing amounts of acetylacetone (0.01–0.08M) at a constant ionic strength μ=0.1 ($NaNO_3$) and at constant pH 6. The reduction of Zn(II) has been found to be diffusion-controlled and irreversible in the presence of acetylacetonate. $E_{1/2}$ gets shifted to more cathodic potentials with increasing [Acetylacetonate]. The reversible half-wave potential ($E^r_{1/2}$) has been calculated by Gellings method. Zn(II) forms three successive complex species with acetylacetonate viz., $[Zn(Acac)]^+$, $Zn(Acac)_2$] and $[Zn(Acac)_3]^-$ with stability constants log β_1=5, log β_2=10, log β_3=14.30 at 25°. The percentage distribution of Zn(II) in its various forms as a function of ligand concentration has also been presented. The kinetic parameters (αn_a and $k^0_{f,h}$) have been calculated by Koutecky's method.

BRANICA[1,2] and coworkers have undertaken polarographic investigations on acetylacetonate complexes of Cu(II) and Ni(II). However, the polarographic study of Zn(II) acetylacetonate system has not been taken up so far. With this aim in view the present study dealing with the polarography of Zn(II)-acetylacetonate system has been undertaken.

Experimental

Solutions of $ZnCl_2$ and $NaNO_3$ were prepared from reagent grade chemicals in conductivity water. Acetylacetone was of E. Merck, G. R. grade and its aqueous solution was used as ligand. The concentration of Zn(II) in each case was kept at $1\times10^{-3}M$. The concentration of acetylacetonate was calculated from the pH and the pK value[3-5] (8.95) of acetylacetone. As no maximum was encountered in the present study, use of a suppressor was avoided.

A manual polarograph (Toshniwal CLO2) in conjunction with polyflex galvanometer (Toshniwal PL-50) was used. All the measurements were made at 25±0.1°. Purified nitrogen gas was passed through the solutions to remove the dissolved oxygen. Saturated calomel electrode (S.C.E.) was used as a reference electrode. The d.m.e. had the following characteristics (in 0.1M $NaNO_3$, open circuit): m=1.673 mg/sec., t=4.04 sec., $m^{2/3} t^{1/6}$=1.778 $mg^{2/3} sec^{-1/2}$, h_{corr}= 63 cm. The number of electrons (n) involved in the reduction process was determined by millicoulometric method of DeVries and Kroon[6] using d.m.e. as cathode and the mercury pool as anode. The formula used was

$$n_2 = n_1 \left(\frac{\Delta i_{d, cad}}{i_{d, cad}}\right)\left(\frac{i_{d, sub}}{\Delta i_{d, sub}}\right)\frac{V_1\ C_1}{V_2\ C_2}$$

where $i_{d, cad}$ is the original diffusion current (corrected for the residual current) for cadmium solution, V_1 its volume, C_1 its concentration and $\Delta i_{d, cad}$ is the change in diffusion current produced by the electrolysis. $i_{d, sub}$, $\Delta i_{d, sub}$, V_2 and C_2 are the corresponding quantities for the solution of the substance. n_1 and n_2 are the number of electrons involved in the reduction of cadmium and substance at d.m.e. respectively. As the concentration and volume in respect of cadmium and substance were the same $V_1=V_2$=0.3 ml; $C_1=C_2=1\times10^{-3}$ M), the last factor in the above equation is unity. In the present system n was found to be 2.

Results and Discussion

Polarograms of the solution containing $1\times10^{-3}M$ Zn(II) and 0.08 M acetylacetone were taken at different pH values. It was observed that the negative shift in $E_{1/2}$ was maximum at pH 6. On further increasing the pH, Zn(II) gets precipitated and hence pH 6 was chosen for studying the complex formation between Zn(II) and acetylacetone. The concentration of the ligand was varied from 0.01 to 0.08 M. In each case a single well defined diffusion-controlled wave appeared. The plots of i_d vs $h^{1/2}_{corr}$ were found to be linear and passing through the origin, thereby showing the diffusion-controlled nature of the reduction.

On applying various criteria of irreversibility[7-10] it has been found that the reduction of Zn(II) in the presence of increasing concentrations of acetylacetonate is irreversible. However, in the absence of the ligand the reduction of Zn(II) is quasi-reversible.

. Lal and Christian[11] and recently Zutshi and Gupta[12] have suggested a method for determining the composition and stability constants of consecutively formed complex species, undergoing irreversible reduction at d.m.e by determining the value of reversible half-wave potential ($E^r_{1/2}$), by Gellings[13] method. This

method has been followed in the present study and the $E^r_{1/2}$ values as a function of [Acetylacetonate] have been presented in Table 1.

TABLE 1—POLAROGRAPHIC CHARACTERISTICS OF Zn(II)-ACETYLACETONATE SYSTEM μ=0.1 ($NaNO_3$), pH 6, TEMP. 25±0.1°.

[H Acac] M	[Acac⁻]×10⁵ M	$-E_{1/2}$ V (S.C.E.)	$-E^r_{1/2}$ V (S.C.E.)	Slope mV
0	0	1.00	0.98	44.0
0.01	1.122	1.02	1.01	80.6
0.02	2.245	1.04	1.02	80.6
0.04	4.467	1.06	1.025	85.7
0.06	6.607	1.08	1.04	65.0
0.08	8.976	1.10	1.06	44.0

A plot of $E^r_{1/2}$ vs-log [Acetylacetonate] (Fig. 1) is found to be a smooth curve thereby showing formation of consecutive complexes. DeFord and Hume's[14] method modified by Irving[15] has been applied for the calculation of composition and stability constants of the complexes.

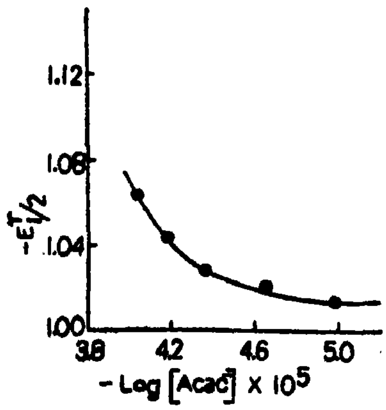


Fig. 1. $-E^r_{1/2}$ vs—log [Acac]⁻ for Zn(II) Acetylacetonate system.

TABLE 2—VALUES OF KINETIC PARAMETERS (αn_a AND $k^0_{f,h}$) FOR THE ELECTRODE REACTION OF Zn(II)-ACETYLACETONATE SYSTEM

[H Acac] M	αn_a	$k^0_{f,h}$ cm/sec
0		
0.01	0.86	3.98×10^{-18}
0.02	0.74	9.22×10^{-14}
0.04	0.74	4.12×10^{-13}
0.06	0.61	1.56×10^{-10}
0.08	0.54	1.78×10^{-10}

An analysis of $F_j[X]$ functions (Fig. 2) reveals the formation of three successive complex species viz., $[Zn(Acac)]^+$, $[Zn(Acac)_2]$ and $[Zn(Acac)_3]^-$ with stability constants $\log \beta_1 = 5$, $\log \beta_2 = 10$ and $\log \beta_3 = 14.30$.

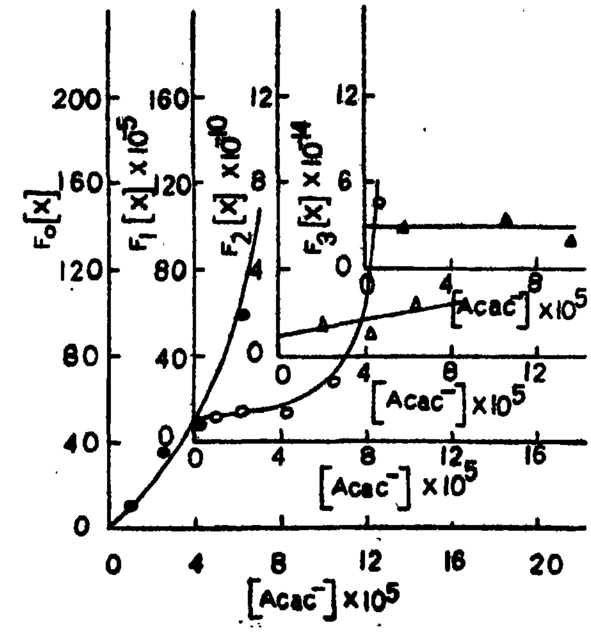


Fig. 2. $F_j[X]$ vs [Acac⁻] for Zn(II) Acetylacetonate system

●—F_0 [X]
○—F_1 [X]
△—F_2 [X]
▲—F_3 [X]

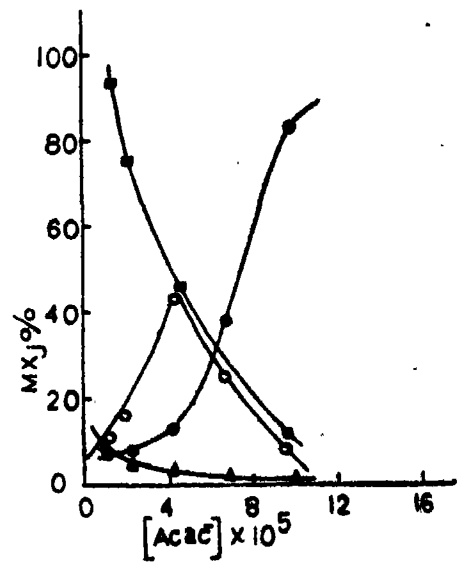


Fig. 3. Percentage distribution of Zn(II) in its various forms as a function of [Acac⁻]

▲—Zn^{2+}
○—$[Zn(Acac)]^+$
■—$[Zn(Acac)_2]$
●—$[Zn(Acac)_3]^-$

The kinetic parameters, αn_a and $k^0_{f,h}$ of the electrode reaction have been calculated by Koutecky's method and the values have been listed in Table 2.

The percentage distribution of Zn(II) in its various forms as a function of [Acetylacetonate] has been presented in Fig. 3.

Acknowledgement

We thank Dr. S. N. Srivastava, Ph.D. (Luck.), Ph.D. (Cantab.), D.Sc.(Luck.), FNAC, FRIC (London), Principal, Agra College, Agra for providing facilities and encouragement.

References

1. M. Petek, Lj. Jeftic and M. Branica, "Polarography 1964", Vol. I (Proceedings IIIrd Intern. Congr. Southampton) Edit. G. J. Hills MacMillan, London 1966, p. 491.
2. B. Cosovic, M. Verzi and M. Branica, *J. Electroanal. Chem.*, 1969, **22**, 325.
3. G. Schwarzenbach and K. Lutz, *Helv. Chim. Acta*, 1940, **23**, 1147.
4. W. Walisch and A. H. Ruppersberg, *Ann. Univ. Saraviensis*, 1950, **8**, 1.
5. M. L. Eidinoff, *J. Amer. Chem. Soc.*, 1945, **67**, 2072.
6. T. DeVries and J. L. Kroon, *J. Amer. Chem. Soc.*, 1953, **75**, 2484.
7. L. Meites, "Polarographic Techniques" (Interscience Publ., New York), 1965, p. 232.
8. R. Goto and I. Tachi, *Proc. Intern. Polarogr. Congr. Prague*, 1951, **1**, 69.
9. P. Delahay, *J. Amer. Chem. Soc.*, 1951, **73**, 4944.
10. P. Kivalo, K. B. Oldham and H. A. Laitinen, *J. Amer. Chem. Soc.*, 1953, **75**, 4148.
11. S. Lal and G. D. Christian, *J. Fur. Praktische Chemie*, 1971, **1**, 99.
12. Kamala Zutshi and K. C. Gupta, *Indian J. Chem.*, 1978, **16A**, 453.
13. P. J. Gellings, *Z. Electrochem. Bur Bunsenges Phys. Chem.*, 1962, **66**, 477, 481, 799 ; 1953, **67**, 167.
14. D. D. DeFord and D. N. Hume, *J. Amer. Chem. Soc.*, 1951, **73**, 5321.
15. H. Irving, "Advances in Polarography" (Ed. I. S. Longmuir) Vol. I. Pergamon Press, London, 1960, p. 42.

J. Indian Chem. Soc.,
Vol. LVII, May 1980, pp. 524-526

Studies on the Interaction Between Iodine and the NN'-Dioxides of Some Twin-Site Donors*

U. MURALIKRISHNA and N. SOMESWARA RAO

Department of Chemistry, Andhra University, Waltair-530 003

Manuscript received 29 March 1979, revised 29 October 1979, accepted 18 March 1980

The –C=N–N=C– group is well known to be a potential donor in metal complexes with the stability order depending on the benzenoid rings attached to it. For example the stability order is 1, 10-phenanthroline 2, 2-bipyridine pyrazine.

The interaction of these compounds with electron acceptor iodine, is found to be similar. This articles presents the studies of the NN'-dioxides of these donors with iodine. Equilibrium constants and IR data on these systems have been presented.

It has been shown that the bonding strength of the donors posessing the –C=N–N=C– is of the order 1,10-phenanthroline > 2,2'-bipyridine > pyrazine in their interaction with the accepter iodine in non-polar solvent carbontetrachloride[1]. The study of the interaction between the NN'-dioxides of these twin-site donors with iodine has not so far been studied. As these NN'–dioxide are very slightly soluble in nonpolar solvents, it is proposed to study the interaction between the NN'-dioxides and iodine in aqueous medium and the solids obtained as result of the reaction between NN'-dioxides and iodine by IR spectroscopy.

Experimental

2,2'-bipyridine NN'-dioxide[2,3], 1,10-phenanthroline-NN' dioxide[4], and pyrazine NN'-dioxide[5,6] were prepared by the methods already reported. The authenticity of the samples was established from its melting point, elemental analysis and IR data. The products were found to be chromatographically homogeneous.

All the UV-visible spectra were recorded on Unicam SP-7(0 recording spectrophotometer provided with temperature control equipment (± 0.5°). 1.0 cm matched quartz cells were used for making spectral measurements. IR spectra were recorded on Carl Zeiss (Jena) UR-10, IR spectrophotometer.

Stock solutions of iodine[7] and the NN'-dioxides were prepared by weighing and dissolution in water. Equilibrium constants for these systems have been determined following the method of Sliffkin[8].

Results and Discussion

From Fig. 1 it can be seen that the spectrum of iodine in water exhibits the absorption of the triiodide ion and solvated iodine molecule. Katzin[9] has reported that the triiodide formation may be due to the following reaction.

$$I_2 \longrightarrow I^+ + I^- \quad \text{... [1]}$$

$$I^- + I_2 \longrightarrow I_3^- \ \textit{Fast} \quad \text{... [2]}$$

Iodine in nonpolar solvents has a peak at 520 nm[10]. The peak at 455 nm is the blue shifted iodine band in water, when the donor concentration is increased, it can be seen from Fig. 1, that there is an increase in the I_3^- absorbance (365) with a simultaneous decrease

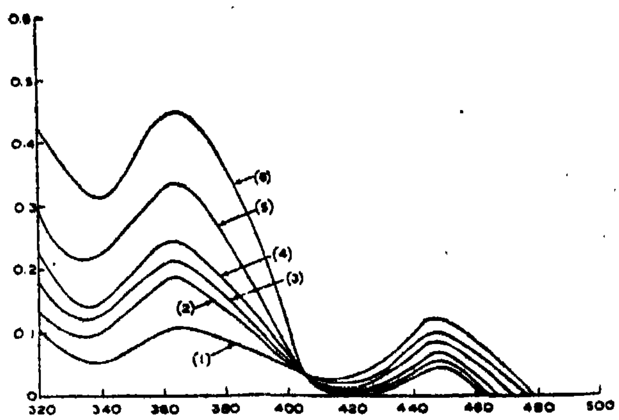


Fig. 1. Absorption Spectrum of Pyrazine NN'-dioxide–iodine in aqueous medium.

X—axis—Wavelength in nm.

Y—axis—Absorbance

1. Iodine in water
2. 2.58×10^{-3} *M* pyrazine NN'-dioxide (PYND) in (I)
3. 5.16×10^{-3} *M* PYND in (I)
4. 7.74×10^{-3} *M* PYND in (I)
5. $10.3\ \times10^{-3}$ *M* PYND in (I)
6. $12.9\ \times10^{-3}$ *M* PYND in (I)

*Presented at the Annual Convention of Chemists held at Andhra University, Waltair during December 1978.

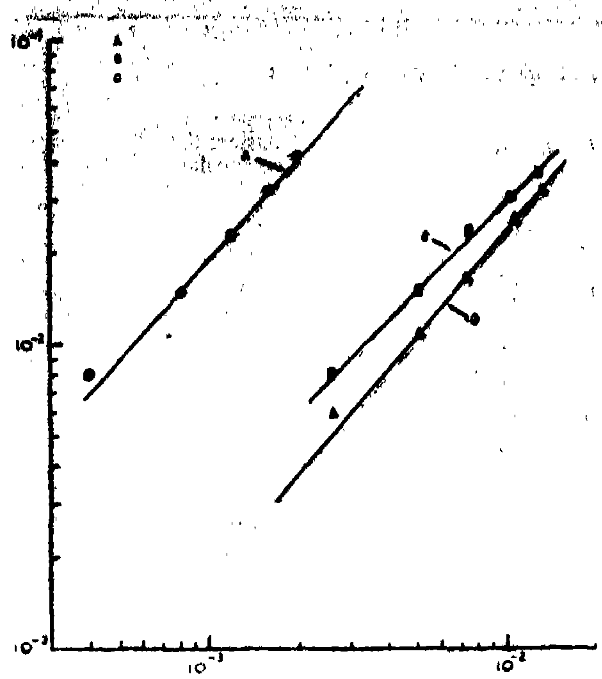


Fig. 2. Plot of Optical Density at 365 nm versus concentration of base

X—axis—consentration – M

Y—axis—Optical Density

(A) 1,10-Phenanthroline NN′-Dioxdc

(B) 2,2′-Bipyridine NN′-Dioxide

(C) Pyrazine NN′-Dioxide

of the 455 nm band. The plot of the log (A) (A=absorbance) against log (D) (D=concentration) is linear with a slope equal to unity (Fig. 2). This suggests that the complex formed is 1 : 1 which derives support from the following points.

1. Linearity in the I_3^- absorbance values with donor concentration.

2. Isosbestic point at 405 nm (Fig. 1.)

The equilibrium constant values are calculated employing the following equation [8,11].

$$K = \frac{C_1(D_0 - D_2) + C_2(D_1 - D_0)}{C_1C_2\,(D_2 - D_1)} \qquad \text{... [3]}$$

where D_0, D_1, D_2 are the optical densities measured at a fixed wavelength with constant iodine concentration and C_1 and C_2 are varying concentrations of donor respectively. The data are presented in Table 1. The wide scatter in K values may be due to hydrogen bonding of these donors in aqueous medium.

From the above considerations the interaction between the donors and iodine can be represented

Table I(A)—Calculation of Equilibrium Constants

S. No.	System	No. assigned in the mixture.	Concentration of the base ($10^{-3}M$)	Absorbance at 365 nm (D)
1.	Pyrazine NN′-dioxide + Iodine	0	0.00	0.12
		1	2.58	0.18
		2	5.16	0.23
		3	7.74	0.29
		4	10.32	0.38
		5	12.91	0.45
2.	2,2′-bipyridine NN′-dioxide + Iodine	0	0.00	0.12
		1	2.58	0.20
		2	5.16	0.27
		3	7.74	0.36
		4	10.33	0.42
		5	12.91	0.49
3.	1,10-phenanthroline NN′-dioxide + Iodine.	0	0.00	0.12
		1	0.40	0.20
		2	0.80	0.27
		3	1.21	0.34
		4	1.61	0.44
		5	2.62	0.54

TABLE I(B)—CALCULATION OF EQUILIBRIUM CONSTANTS

S. No.	System		Mixtures	Equilibrium constant K (litres/mole)
1.	Pyrazine NN'-dioxide + Iodine		012	29.70
			013	41.09
			014	24.22
			015	18.08
			023	72.10
			024	28.50
			025	20.95
			034	52.38
			035	29.70
			045	72.52
		Average		38.92
2.	2,2'-bipyridine-NN'-dioxide + Iodine		012	85.72
			013	38.71
			014	27.27
			015	20.55
			023	55.59
			024	53.70
			025	36.30
			034	80.13
			035	45.86
			045	82.40
		Average		52.62
3	1,10-phenanthroline NN'-dioxide + Iodine		012	547.54
			013	258.28
			014	164.88
			015	119.27
			023	468.84
			024	225.50
			025	145.62
			034	430.56
			035	209.11
			045	405.61
		Average		297.52

by[10].

$$B + I_2 \rightleftharpoons BI_2 \quad \dots [4]$$

$$BI_2 \rightleftharpoons BI^+ + I^- \quad \dots [5]$$

$$I^- + I_2 \rightleftharpoons I_3^- \quad \dots [6]$$

The above scheme is analogous to the interaction of iodine with the original base in nonpolar solvents[1].

The interaction[7,8] of the aromatic amines, aminoacids, proteins and β-carotene with iodine in nonpolar solvents is reported to take place through the formation of outer complex with the subsequent transformation of this to inner complex.

Further, the solids obtained by the interaction of these NN'-dioxides with iodine in aqueous solution and slow evaporation of the solvent under low pressure showed the presence of iodine as evidenced by the characteristic 360 nm band. This supports the idea that iodine in the final product is in the ionic form[8]. That the solids obtained contain iodine in the ionic form is further confirmed by the well known starch-iodine reaction.

The methanolic solutions of the donors with iodine also gave the characteristic 360 nm band (iodine $1.9 \times 10^{-5} M$ + saturated solutions of the donors) indicating the ionic form of iodine to be present in this medium. However, in chloroform the shifted iodine bands are observed (with saturated solutions of the donors + iodine $8.92 \times 10^{-4} M$ keeping same concentration of iodine as reference).

1,10-phenanthroline NN'-dioxide	—	485 nm
2,2'-bipyridine NN'-dioxide	—	500 nm
Pyrazine NN'-dioxide	—	505 nm

IR Spectra of the solids :

All the solids between these NN'-dioxides and iodine are prepared by mixing equimolar solutions of

the donor and iodine, and the water removed slowly[1] at reduced pressure. The IR spectra were taken in nujol mull.

From the IR spectral data (Table 2) of the above solid complexes it can be seen that the $\nu_{N\to O}$ of the NN'-dioxides shift to lower frequency on complex formation. Further the stretching frequency difference $\Delta\nu_{N\to O}$ is in the following order. 1,10-phenanthroline NN'-dioxide > 2,2'-bipyridine NN'-dioxide≈pyrazine NN'-dioxide.

this fact is supported by the presence of two very strong >N→O stretching absorption at 1262 cm^{-1} and 1255 cm^{-1} in its IR spectrum. However, on complexation the 1265 cm^{-1} and 1255 cm^{-1} bands are found to shift to 1235 cm^{-1} and 1228 cm^{-1} respectively. The similar trend in the shift of >N→O bending vibrations is also observed. In the case of pyrazine NN'-dioxide the bands appearing at 1270^{-1} and 880 cm^{-1} which can be assigned to >N→O stretching vibration and bending vibration respectively shift to lower frequencies (1240 cm^{-1} and 845 cm^{-1}) on complex formation. In the case of 1, 10-

Table 2—Observed N - O Frequencies of Some NN'-dioxides and their Iodine Complexes

S. No.	Compounds	N–O stretch (cm^{-1})	N–O bend (cm^{-1})
1.	Pyrazine NN'-dioxide	1270	889
2.	Pyrazine NN'-dioxide+Iodine	1240	845
3.	2,2'-bipyridine NN'-dioxide	1265 1255	855 840
4.	2,2'-bipyridine NN'-dioxide + Iodine	1235 1228	835 815
5.	1,10-phenanthroline NN'-dioxide	1255 1210 (Sh)	864 856 (Sh)
6.	1,10-phenanthroline NN'-dioxide+Iodine	1215 1200 (Sh)	848 832 (Sh)

Sh—Shoulder

The active site of the >N → O bond for complex formation with iodine is presumably the oxygen atom, as the stretching frequency of >N → O bond shifts to lower frequency in all the cases. The shift of $\nu_{N\to O}$ to lower frequeney seems to be ascribable to charge transfer from an oxygen n-type orbital to the iodine σ^-_u-antibonding orbital, which decreases the electron density at the oxygen atom so that the π-electron resonance interaction of the oxygen 2p π-electrons with the rest of the π-system is weakened.

Kubota *et al*[13] and Kulevesky and Severson[14] reported similar changes in the stretching frequency of >N → O bond on complexation with iodine in the case of aromatic N-oxides in organic solvents.

Simpson and his co-workers[2,15] observed changes in the >N ⟶ O stretching band to lower frequencies upon complex formation with transition metal. It was argued that the uncoordinated 2,2'-bipyridine NN'-dioxide molecule in the solid state most likely exists in the staggered conformation unlike 2,2'-bipyridine and phenanthroline NN'-dioxide, two bands appear in the original base at 1255 cm^{-1} (broad) and 1210 cm^{-1} (weak). The two bands are probably due to repulsions of the two >N → O groups leading to somewhat distored configuration. On complexation with iodine the stretching and bending vibrations are shifted to lower frequencies i.e., at 1215 cm^{-1} and 1200 cm^{-1}.

As can be seen from Table 2, the order of the shift of frequency is pyrazine NN'-dioxide ≈2, 2'-bipyridine NN'-dioxide<1,10-phenanthroline NN'-dioxide, similar to that when equilibrium constants in aqueous medium are considered.

References

1. N. Someswara Rao, Ph.D. Thesis, Andhra University, Waltair, 1977.
2. P. G. Simpson, A. Vinciguerra and J. V. Quagliano, *Inorg. Chem.*, 1963, 2, 282.
3. G. M. Badger and W. H. F. Sasse, *J. Chem. Soc.*, 1956, 617.

4. B. B. BRIDGLAND and W. R. MC. GREGER, *J. Inorg. Nuclear Chem.*, 1969, **31**, 43.

5. C. F. KOELSCH and W. H. GUMPRECHT, *J. Org. Chem.*, 1958, **23**, 1603.

6. B. KLEIN and J. BERKOWITZ, *J. Amer. Chem. Soc.*, 1959, **81**, 5160.

7. M. A. SLIFKIN, *Spectrochim. Acta*, 1964, **20**, 1543.

8. M. A. SLIFKIN, *Spectrochim. Acta*, 1965, **21**, 1391.

9. C. I. KATZIN, *J. Chem. Phys.*, 1953, **21**, 490.

10. H. TSUBOMURA and R. P. LANG, *J. Amer. Chem. Soc.*, 1961, **83**, 3085.

11. S. NAGAKURA and J. GOUTERMAN, *J. Chem. Phys.*, 1957, **26**, 881.

12. J. H. LUPINSKI, *J. Phys. Chem.*, 1962, **67**, 2725.

13. T. KUBOTA, K. EZUMI, M. YAMKAWA and Y. MATSUI, *J. Mol. Spectry*, 1967, **24**, 378.

14. N. KULEVSKY and R. G. SEVERSON JR., *Spectrochim. Acta*, 1970, **26**, 2227.

15. A. VINCIGUERRA, P. G. SIMPSON, Y. KAKIULI and J. V. QUAGLIANO, *Inorg. Chem.*, 1963, **2**, 236.

J. Indian Chem. Soc.,
Vol. LVII, May 1980, pp. 529-531

Measurement of Stability Constant and Some Thermodynamic Parameters of Clay Humus System

M. ADHIKARI* and T. K. MUKHOPADHYAY

Physical Chemistry Laboratory, Department of Applied Chemistry, University of Calcutta

Manuscript received 23 February 1979, revised 12 December 1979, accepted 18 March 1980

Stability constants of clay humus complexes are evaluated by an analytical method based on a new approach, and the thermodynamic functions of the products are calculated. The values of the latter indicate the spontaneity of the reaction. The entropy change ($\triangle S$) for clay humus interactions are positive and are moderately high, indicating the chelation phenomena of clay—organic matter interaction as purely an entropy effect.

ALTHOUGH a number of studies[1-3] are reported regarding the nature and relative stability of the products formed by the reaction of metals with humic materials, very little attempt has yet been made to evaluate these in case of clay—humus interaction[4].

This paper reports the determination of a new method to calculate the stability constant values of clay humus interaction products and to derive some thermodynamic parameters in order to get an idea regarding the nature of such interactions in the environment.

Theory :

According to Martell and Calvin[5], the equilibrium reaction for chelation or complex formation can be written as

$$M + nK_s \rightleftharpoons M(K_s)_n \quad \dots (1)$$

where 'M' is the metal ion and 'K_s' is the complexing agent and 'n' the number of moles of the complexing agent that combine with one mol of 'M'. Therefore, the formation constant or equilibrium constant can be expressed as

$$K = \frac{[M(K_s)_n]_{eq}}{[M]_{eq}\,[K_s]^n_{eq}} \quad \dots (2)$$

where $[M]_{eq}$ = Equilibrium concentration.

The calculation of concentrations of unreacted H—Clay and unreacted HA (or FA) are based on the assumption that H-Clay and HA(or FA) in the complexes are so strongly bound that during continuous neutralisation with dilute alkali, the complexes do not suffer any dissociation but only the unreacted H-Clay and HA (or FA) react with alkali.

Let the volume of alkali in ml required to neutralise the unreacted H-Clay and HA(or FA) after complexation $= V_1$ ... (3)

Let the volume of alkali in ml required to neutralise the total amount of HA(or FA) added for complexation) $= V_2$ ... (4)

and let the volume of alkali required in ml to neutralise the total amount of H-Clay used for the complexation $= V_3$ ... (5)

i.e., the total amount of alkali in ml required for both the H-Clay and HA(or FA) when there is no complexation $= V_2 + V_3$

Therefore, the amount of alkali in ml. which is not required when there is complexation between H-Clay and HA(or FA) : $V_4 = [(V_2 + V_3) - V_1]$

The pK_a values of H-Clay and HA(or FA) can be determined from the volumes of alkali required at the half neutralisation point. Knowing the pK_a values of H-Clay and HA(or FA), the relative strength of H-Clay and HA(or FA) species in the reaction system may be evaluated. Since the relative strength of an acid is a measure of its tendency to release the proton, the position of the equilibrium with a given solvent, as determined by the dissociation constant, is an indication of the strength of the acid. Let the ratio of the relative strengths of H-Clay and HA(or FA) be 'Z', then the volume of alkali in ml required for H-Clay (unreacted)

$$= \frac{V_1 \times Z}{1+Z} \quad \dots (6)$$

and the volume of alkali in ml required for HA(or FA) (unreacted)

$$= \frac{V_1 \times 1}{1+Z} \quad \dots (7)$$

If the average molecular weight and the colloid content of H-Clay andthe HA (or FA) are known, then with the help of equations (1), (2) and (3), it is possible to

*Present address : College of Agriculture, Calcutta University.

evaluate the molar concentrations of the unreacted H-clay and HA (or FA) respectively.

Let the value for unreacted H-Clay = X mol litre^{-1} and for the unreacted HA(or FA) = Y mol litre^{-1}.

Before addition of alkali, let the molar concentrations of H-Clay and HA(or FA) in the complexes be X_1 and Y_1 respectively.

Therefore, number of mols litre^{-1} of HA(or FA) reacted = $(X_1 - X)$ and the number of mol litre^{-1} of H-Clay reacted = $(Y_1 - Y)$ for complexation.

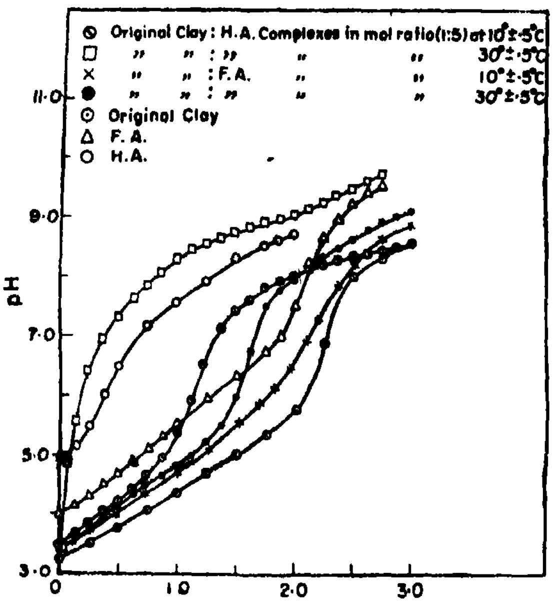


Fig. a

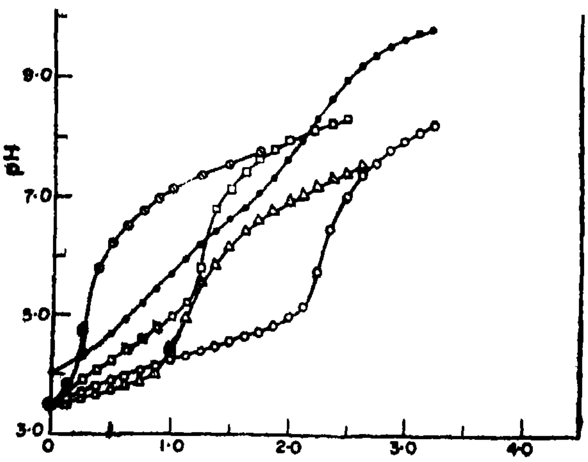


Fig. b

○ Oxide free Clay : F.A. Complexes in mol ratio (1:40) at 10°±.5°C
□ " " : " " " 30°±.5°C
△ " " : H.A. " " (1:42.5) at 10°±.5°C
⊘ " " : " " " " 30°±.5°C
● Oxide Free Clay

Here (H-Clay) is considered like a metal ligand and HA(or FA) as the complexing agent, hence equation (2) takes the form as

$$K = \frac{[Y_1 - Y]}{[X]\,[Y]} \qquad \dots (8)$$

Equations (6) and (7) are made use of in obtaining X, Y and X_1. The values of Z and V_1 are obtained from Figures (a) and (b).

Experimental

The experimental procedure for electrometric titrations of clay—humus interactions is similar to that reported earlier[6]. The titrations were carried out at a fixed ionic concentration (0.1 mol litre^{-1}) at two different temperatures viz. $(10 \pm 0.5)°$ and $(30 \pm 0.5)°$ and at a fixed pH of 4.5, using N/100 sodium hydroxide, B. D. H., GR Grade, as the titrant. The reason for maintaining the pH at lower range was to avoid possibility of release of extra protons, such as those from hydration water of the clay—organic matter system[7].

The log K values of clay—HA(or FA) complexes were obtained by using the equation (8) and the thermodynamic parameters were derived from the following relations :

$$\Delta G = -RT \ln K \qquad \dots (9)$$

$$\Delta G = \Delta H - T\,\Delta S \qquad \dots (10)$$

and $$\frac{d \ln K}{dT} = \Delta H/RT^2 \text{ (using the integrated form)} \qquad \dots (11)$$

The results are given in Table 1 and 2.

TABLE 1 – STABILITY CONSTANT OF H-CLAY – HA(or FA) COMPLEXES

H-Clay and HA(or FA) complexes in molar ratio	Temperature maintained T = (283 ± 0.5)A	Temperature maintained T = (303 ± 0.5)A
Original H-Clay – HA(1:5)	9.10	9.90
Oxide free H-Clay – HA(1:42.5)	8.00	8.60
Original H-Clay – FA(1:12)	5.90	7.90
Oxide free H-Clay – FA(1:60)	5.60	6.66

(HA and FA denote humic and fulvic acids respectively)

TABLE 2—THERMODYNAMIC PARAMETERS FOR H-CLAY – HA(or FA) COMPLEXES

H-Clay and HA(or FA) complexes in molar ratio	(T±0.5) A	$-\Delta G \times 10^{*}$ kJ. mol^{-1}	$\Delta H \times 10^{*}$ kJ. mol^{-1}	$\Delta S \times 10^{*}$ kJ. mol^{-1}A^{-1}
Original H-Clay – HA(1:5)	283	5.2295	3.0230	.29160
	303	5.8127		
Oxide free H-Clay – HA(1:42.5)	283	4.9244	2.5946	.26568
	303	5.4558		
Original H-Clay – FA(1:12)	283	4.2033	10.4730	.51859
	303	5.2405		
Oxide free H-Clay – FA(1:60)	283	4.0797	6.2195	.36392
	303	4.8076		

Discussion

The higher value of the stability constant (vide Table 1) of original H-Clay—HA complex than that for original H-Clay-FA system indicates a greater stability of the former. The removal of the sesquioxides coating decreases the stability constant value, which suggests the greater complexing ability of the sesquioxides groups. The stability constant values for the complexes increase with increase in temperature. This is due to partial removal of hydrated water molecules from the clay surfaces with rise in temperature, which makes available more of complexing sites to the clay surfaces for interaction.

The values of free energy ($\triangle$G)–, enthalpy ($\triangle$H)–, and entropy ($\triangle$S)—changes for different clay—organic matter interaction products are given in Table 2. A comparison of these results reveals that the free energies of formation of the complexes are negative in all the cases, indicating the process of interaction to be spontaneous. The values of $\triangle$H in all the cases (vide Table 2) are positive, indicating an absorption of energy during interactions. $\triangle$H has been calculated (equation 11) by assuming it to remain constant over a temperature range from 10° to 30° for a given complexation process (e. g., that between original H-Clay and FA or oxide free H-Clay and HA etc.), although such $\triangle$H values are obviously different for different complexation processes over the same range of temperatures.

The entropy changes ($\triangle$S), accompaning the formation of complexes, are positive and greater than ΔH (which are also positive) in all the cases ; this goes to emphasise that such chelation reaction is an "entropy—controlled" effect. The moderately high values of $\triangle$S indicate the strong complexing ability of humic materials towards clays. The values of the stability constant and the thermodynamic parameters are less for oxide free H-Clay—HA(or FA) species in incomparison with those for the original H-Clay. This is due to a high bonding ability of the sesquioxides coatings of clays with the humic fractions.

From the more or less similar values of the thermodynamic parameters for different soil humus species, it appears that the nature and the stereochemistry of the different functional groups of the legands taking part in such complexations, are almost identical. This corroborates the earlier findings by Infrared spectral study of Clay humus systems.

Acknowledgement

One of the authors (T. K. M.) is thankful to C. S. I. R., New Delhi, for the award of a Post Doctoral Fellowship.

References

1. G. SCHWARZENBACH, *Chimia.*, 1949, 3, 1.
2. M. ADHIKARI, G. CHAKRAVARTY and G. C. HAZRA, Measurement of Stability Constants of Humic Acid Metal Complexes, *Acta. Agronomica*, 1977, 21, 134.
3. F. J. STEVENSON, *Soil. Sci. Soc. Am. Proc.*, 1972, 36, 884.
4. D. J. GREENLAND, *Soils. Fertil.*, 1965, 28, 415, 521.
5. A. E. MARTELL and M. CALVIN, 'Chemistry of Metal Chelate Compounds', Prentice Hall, Inc, N. Y. (1952).
6. M. ADHIKARI, T. K. MUKHERJEE and G. CHAKRAVARTY, Electrometric Studies on Clay—Fulvic Acid Interactions, *J. Indian Chem. Soc.*, 1976, 53, 1233.
7. F. J. STEVENSON, *Soil. Science*, 1977, 10, 123.
8. M. ADHIKARI and T. K. MUKHOPADHYAY, Infrared Absorption Spectra of Clay—Humus and Metal—Clay Humus Complexes, *J. Indian Soc. Soil. Sci.*, 1980, 57, 73.

J. Indian Chem. Soc.,
Vol. LVII, May 1980, pp. 532-535

Studies in the Synthesis of Furochromones. Part VII

R. J. PATOLIA and K. N. TRIVEDI

Chemistry Department, Faculty of Science, M. S. University of Baroda, Baroda-390 002

Manuscript received 22 August 1979, accepted 4 March 1980

2-Hydroxy-5-allyloxyacetophenone(Ia), on Claisen condensation with ethyl formate in the presence of sodium yielded 2-hydroxy-2,3-dihydro-6-allyloxychromone (IIa), which on dehydration and Claisen rearrangement gave 5-allyl-6-hydroxychromone (IVb). Cyclization of (IVb) with conc. sulphuric acid afforded 2-methyl-2,3-dihydro-4H-furo (3,2-f) benzopyran-4-one (Va). This on dehydrogenation with palladised charcoal furnished 2-methyl-4H-furo(3, 2-f) benzopyran-4-one(VIa). 4H-Furo (3, 2-f) benzopyran-4-one(VIb) was synthesised from (IVb) by carrying out oxidation with osmium tetroxide and potassium periodate, followed by cyclization with PPA. Similarly, 2,9-dimethyl-4H-furo (3,2-f)-benzopyran-4-one (VIc) and 9-methyl-4H-furo (3, 2-f) benzopyran-4-one (VId) were synthesised from 2-hydroxy-4-methyl-5-allyloxyacetophenone (Ic). (Ic) was prepared from 2,5-dihydroxytoluene through acetylation and Fries migration.

IN continuation of our work[1] we report here the synthesis of four new furochromones, viz. 2-methyl-4-H-furo(3,2-f)benzopyran-4-one (VIa), 4H-furo(3,2-f) benzopyran-4-one (VIb), 2, 9-dimethyl-4H-furo(3,2-f) benzopyran-4-one (VIc) and 9-methyl-4H-furo (3,2-f) benzopyran-4-one (VId).

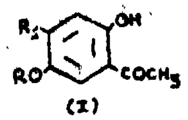
Claisen condensation of 2-hydroxy-5-allyloxyacetophenoe (Ia)[2], with ethyl formate in the presence of pulverized sodium, gave 2-hydroxy-2, 3-dihydro-6-allyloxychromone (IIa). It gave pale red brown colour with alcoholic ferric chloride after one minute. IR spectra: 3250 cm^{-1} (-OH), 1645 ($>C=O$); UV λ_{max}^{MeOH} : 224 nm (log ε 4.67), 339 (3.94); (MeOH + NaOH), 228 (4.63), 338 (4.28). It was dehydrated to corresponding chromone derivative (IVa), by using aqueous sulphuric acid. Claisen rearrangement of (IVa) gave 5-allyl-6-hydroxychromone (IVb), which on trituration with conc. sulphuric acid yielded 2-methyl-2,3-dihydro-4H-furo(3, 2-f)benzopyran-4-one(Va). The structure of which was confirmed by NMR : δ, 1.46, doublet, 3H, J=7Hz, CH_3 group at C_2-CH_3 ; 3.12-3.98, multiplet, 2H, two methylene protons at C_3-H_2 ; 4.86-5.11, multiplet, 1H, methine proton at C_2-H ; 6.11 doublet, 1H, J=7Hz, C_8-H ; 6.91, doublet, 1H, J=9Hz, C_9-H, 7.12 doublet, 1H, J=9Hz, C_6-H, 7.61, doublet, 1H, J=7Hz, C_8-H. This spectral data confirmed that the Claisen rearrangement of 6-allyloxychromone (IVa) took place at five position, and not at seven position; in the latter case, spectrum of cyclized product would have shown two singlets in the aromatic region instead of two doublets, each for one aromatic proton. Dehydrogenation of (Va) was done with palladised charcoal in boiling diphenyl ether to yield 2-methyl-4H-furo(3,2-f)-benzopyran-4-one (VIa).

The compound (IVb), on treatment with osmium tetroxide-potassium periodate in ethyl acetate, followed by cyclization of 5-acetaldehydo product with polyphosphoric acid gave 4H-furo-(3,2-f)benzopyran-4-one (VIb).

2,5-Dihydroxytoluene when treated with acetic anhydride and pyridine gave an ester 2,5-diacetoxytoluene. The ester on Fries migration by using anhydrous aluminium chloride, converted 2,5-dihydroxy-4-methylacetophenone (Ib). The structure of (Ib) was confirmed on the basis of NMR spectrum obtained for the compounds (IIb) and (IVb). The ketone (Ib), was subjected to allylation with allyl bromide and anhydrous potassium carbonate to give 2-hydroxy-4-methyl-5-allyloxyacetophenone (Ic), which on Claisen condensation with ethyl formate in presence of pulverized sodium yielded 2-hydroxy-2, 3-dihydro-6-allyloxy-7-methylchromone (IIb). IR spectra : 3180 cm^{-1} (-OH), 1660 ($>C=O$); NMR (DMSO-d_6), δ, 2.23 singlet, 3H, CH_3 group at C_7CH_3 ; 2.67-2.93 multiplet, 2H, two methylene protons at C_3-H_2 ; 4.54, doublet, 2H, J=6Hz, -OCH_2CH=CH_2 ; 5.17-5.55, multiplet, 2H, -$OCH_2CH=CH_2$; 5.75, triplet, 1H, at C_2-H ; 5.85-6.24, multiplet 1H, -$OCH_2CH=CH_2$; 6.88, singlet, 1H, C_8-H ; 7.14, singlet, 1H, C_5-H ; This spectral data confirmed the cyclic structure (IIb) and not the ring open structure 3-(2-hydroxy-4-methyl-5-allyloxy-phenyl)-3-oxopropanal (III). Besides this, there are two singlets in the aromatic region, which confirmed the ketone structure of (Ib).

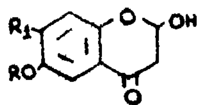
The compound (IIb), on dehydration, followed by Claisen rearrangement and cyclization with conc. sulphuric acid gave 2,9-dimethyl-2,3-dihydro-4H-furo (3,2-f) benzopyran-4-one (Vb). Dehydrogenation of (Vb) by pliadised charcoal (10%) furnished 2,9-dimethyl-4H-furo(3,2-f) benzopyran-4-one (VIc).

The reaction of (IVa), with osmium tetroxide and potassium periodate in ethyl acetate followed by cyclization with PPA, yielded 9-methyl-4H-furo(3,2-f) benzopyran-4-one(VId). The NMR spectra for the compounds (VIa, b, c and d) are given after the experimental procedure of each.



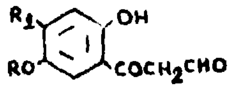
(I)

(Ia) R = $-CH_2CH=CH_2$, R_1 = H
(Ib) R = H, R_1 = CH_3
(Ic) R = $-CH_2CH=CH_2$, R_1 = CH_3



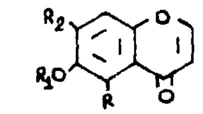
(II)

(IIa) R = $-CH_2CH=CH_2$, R_1 = H
(IIb) R = $-CH_2CH=CH_2$, R_1 = CH_3



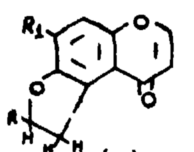
(III)

(III) R = $-CH_2CH=CH_2$, R_1 = CH_3



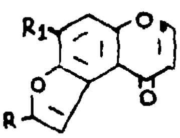
(IV)

(IVa) R = R_2 = H, R_1 = $-CH_2CH=CH_2$
(IVb) R = $-CH_2CH=CH_2$, R_1 = R_2 = H
(IVc) R = H, R_1 = $-CH_2CH=CH_2$, R_2 = CH_3
(IVd) R = $-CH_2CH=CH_2$, R_1 = H, R_2 = CH_3



(V)

(Va) R = CH_3, R_1 = H
(Vb) R = R_1 = CH_3



(VI)

(VIa) R = CH_3, R_1 = H
(VIb) R = R_1 = H
(VIc) R = R_1 = CH_3
(VId) R = H, R_1 = CH_3

Experimental

Unless otherwise stated NMR spectra were taken in $CDCl_3$ solution on a 90 MHz spectrometer with TMS at an internal standard. The IR spectra (nujol) were determined with Perkin-Elmer 457 grating spectrophotometer. The UV spectra were recorded on Beckmann DU-2 spectrophotometer.

2-Hydroxy-2,3-dihydro-6-allyloxychromone (*IIa*) :

Pulverized sodium (1.15 g) was kept in dry ether (5 ml) in a flask fitted with water condenser and maintained with stirring at 20° for 1½ hr. During this time the solution of 2-hydroxy-5-allyloxyacetophenone[8] (1.92 g) in ethyl formate (16 ml) was added drop by drop as to react with sodium. When the reaction had subsided, more ethyl formate (8 ml) was added, and the reaction mixture was refluxed at 65° for 10 minutes. It was then left for two days. Alcohol and water were successively added with care and the resulting alkaline solution was extracted twice with ether. The aqueous alkaline layer was acidified with cold dilute acetic acid. A crystalline brown solid separated slowly was filtered and washed with water. It crystallised from benzene as colourless small prisms, m.p. 114°, yield 1.2 g. After one minute it gave red-brown colour with alcoholic ferric chloride and colour became more fast on standing. (Found : C, 65.43 ; H, 5.41 ; $C_{12}H_{12}O_4$ requires C, 65.45 ; H, 5.45%).

6-Allyloxychromone (*IVa*) :

2-Hydroxy-2,3-dihydro-6-allyoxychromone (2 g) was taken with dilute sulphuric acid (30%, 60 ml) in a flask and heated on water bath for 2 hr. After cooling, the pasty product was separated, washed with water and sodium bicarbonate solution, and purified by passing it over a column of active basic alumina using petroleum ether (b.p. 60-80°) as eluent. It crystallised as pale yellow needless from petroleum ether, m.p. 64°, yield 1.3 g. (Found : C, 71.78 ; H, 5.11 ; $C_{12}H_{10}O_3$ requires C, 71.28 ; H, 4.95%).

5-Allyl-6-hydroxychromone (*IVb*) :

6-Allyloxychromone (1 g) was refluxed with dimethylaniline (6 ml) for 80 minutes ; after cooling the reaction mixture was poured into ice containing hydrochloric acid (20 ml). The separated product was treated with sodium hydroxide solution, filtered and acidified with dil. hydrochloric acid. The product was chromatographed on silica gel, using benzene chloroform (4:1) mixture as an eluent. It crystallized as colourless shining thick needles from benzene, m.p. 186°, yield 0.8 g. (Found : C, 71.15 ; H, 4.71 ; $C_{12}H_{10}O_3$ requires C, 71.28 ; H, 4.95%). IR spectra : 3180 cm^{-1}(OH), 1635 (C=O).

2-Mthyl-2,3-dihydro-4H-furo(3,2-f) benzopyran-4-one (*Va*) :

5-Allyl-6-hydroxychromone (0.6 g) was triturated with sulphuric acid (85 %, 6 ml) in a water bath for 12 minutes, the contents was poured into crushed ice, the separated product was filtered and washed with dil. sodium hydroxide solution. It crystallized from petroleum ether as cream coloured needles, m.p. 123-24°, yield 0.4 g. (Found : C, 71.76 ; H, 5.40 $C_{12}H_{10}O_3$; requires C, 71.28 ; H, 4.95%).

2-*Methyl-4H-furo(3,2-f)benzopyran-4-one* (*VIa*) :

A mixture of 2-methyl-2,3-dihydro-4H-furo(3,2-f)-benzopyran-4-one (0.3 g), palladised charcoal (10%, 0.5 g) and diphenyl ether (5 ml) was refluxed for 8 hr. The reaction mixture was filtered hot and the filtrate steam distilled to remove diphenyl ether. The remaining residue was extracted with ethyl acetate, evaporated and chromatographed on silica gel. Elution with petroleum ether-benzene (7:3) gave the product (0.16 g). It crystallized from ethanol as colourless small needles, m.p. 134°. (Found : C, 71.97 ; H, 4.50 ; $C_{12}H_8O_3$

requires C, 72.00; H, 4.00%). UV λ_{max}^{MeOH} : 227 nm (log e 4.64), 265 nm (log e 4.28), 294 nm (log e 4.28), 328 nm (log e 4.31); NMR, δ, 2.53 (s, 3H, C_2-CH_3), 6.33 (d, 1H, J=7Hz, C_3-H), 7.22 (d, 1H, J=9Hz, C_9-H), 7.42 (s, 1H, C_3-H), 7.65 (d, 1H, J=9Hz, C_8-H), 7.85 (d, 1H, J=7Hz, C_6-H).

4H-furo(3,2-f) benzopyran-4-one (VIb) :

5-Allyl-6-hydroxychromone (0.6 g) in ethyl acetate (80 ml) and osmium tetroxide (60 mg) in water (30 ml) were vigorously stirred for 15 minutes. Potassium periodate (1.5 g) was added in small quantities to the dark solution over a period of 2 hr. The reaction mixture was stirred 1 hr more. The ethyl acetate layer was separated, washed with water and dried with sodium sulphate and distilled. The residue, 5-acetaldehydo product was taken in PPA (12 ml) and heated in an oil bath for 1 1/2 hr at 115°. It was then poured over ice. The separated solid was extracted with ethyl acetate, washed successively with very dil. sodium hydroxide solution and water, dried with sodium sulphate and the solvent distilled off. The crude product was dissolved in benzene (1.5 ml) and percolated through a column of silica gel. Elution with petroleum ether-benzene (2:3) yielded VIb (0.14 g), which crystallized from benzene-petroleum ether as colourless needles, m.p. 188° (Found : C, 70.49; H, 3.32, $C_{11}H_6O_3$ requires C, 70.98; H, 3.23 %). UV λ_{max}^{MeOH} : 262 nm (log e 4.22), 291 nm (log e 4.26), 318 nm (log e 4.27); NMR : δ, 6.38 (d, 1H, J=6Hz, C_6-H), 7.29 (d, 1H, J=2Hz, C_1-H), 7.35 (d, 1H, J=9Hz, C_9-H), 7.7-7.9 (m, 3H, C_2-H, C_6-H and C_8-H).

2,5-Dihydroxy-4-methylacetophenone (Ib) :

2,5-Diacetoxytoluene m.p. 49-50° (4.16 g) prepared from 2,5-dihydroxytoluene by the action of acetic anhydride in presence of pyridine, was thoroughly mixed with anhydrous aluminium chloride (8.0 g) and the mixture slowly heated in an oil bath at 100° for 1 hr and then at 120° for 1½ hr more. The solid contents were poured into a beaker containing crushed ice (200 g) and conc. hydrochloric acid (20 ml) when the solid product separated out, was filtered and washed with water, dissolved in (8%) sodium hydroxide solution. The filtrate on acidification with hydrochloric acid gave 2,5-dihydroxy-4-methylacetophenone (1.8 g). It was crystallized from aqueous ethanol, m. p. 148-49°. (Found : C, 65.50; H, 5.74; $C_9H_{10}O_3$ requires C, 65.06; H, 6.02%). IR : 3110 cm^{-1} (-OH), 1645 (>C=O).

2-Hydroxy-4-methyl-5-allyloxyacetophenone (Ic) :

A mixture of 2,5-dihydroxy-4-methylacetophenone (3.32 g), anhydrous potassium carbonate (10 g) and allyl bromide (1.8 ml) in dry acetone (80 ml) was refluxed on a water bath for 8 hr. After the evaporation of acetone the remaining solution was acidified by dil. hydrochloric acid, and extracted with ether. The ethereal layer was shaken with 12% sodium hydroxide solution and the separated sodium salt was filtered. It was then acidified and extracted with ether. On evaporation of ether greenish yellow colour liquid was obtained which was used for further reaction.

2-Hydroxy-2,3-dihydro-6-allyloxy-7-methylchromone (IIb) :

The solution of 2-hydroxy-4-methyl-5-allyloxyacetophenone (3.0 g) in ethyl formate (16 ml) was allowed to react slowly with pulverized sodium (1.72 g) kept in dry ether (5 ml) at 15° for 1 hr. More ethyl formate (9 ml) was added as usual, and the reaction mixture was refluxed in a water at 55° for 15 minutes and left overnight. It crystallised from aqueous ethanol as colourless needles, m.p. 142° (decom.), yield 1.7 g. It did not give any colouration with alcoholic ferric chloride even on keeping for long time. (Found : C, 67.08; H, 5.98; $C_{13}H_{14}O_4$ requires C, 66.67; H, 5.98%). UV λ_{max}^{MeOH} ; 228 nm(log e 4.80), 324 nm(log e 4.22); (MeOH + NaOH) 227 nm (log e 4.37); 324 nm (log e 4.20).

6-Allyloxy-7-methylchromone (IVc) :

2-Hydroxy-2, 3-dihydro-6-allyloxy-7-methylchromone (1.8 g) was dehydrated by using dilute sulphuric acid (30%, 50 ml) in a water bath for 90 minutes. It crystallised as colourless shining needles, m.p. 80-82°, yield 1.1 g. (Found : C, 72.11; H, 5.62; $C_{13}H_{12}O_3$ requires C, 72.21; H, 5.55%). NMR : δ, 2.33 (s, 3H, C_7-CH_3), 4.58 (d, 2H, J=6Hz, -OCH_2CH=CH_2), 5.17-5.49 (m, 2H, -OCH_2CH=CH_2), 5.81-6.14 (m, 1H, -OCH_2CH=CH_2), 6.20 (d, 1H, J=6Hz, C_3-H), 7.14 (s, 1H, C_8-H), 7.38 (s, 1H, C_5-H) 7.67 (d, 1H, J=6Hz, C_2-H).

5-Allyl 6-hydroxy-7-methylchromone (IVd) :

5-Allyloxy-7-methylchromone (1.5 g) was refluxed with dimethylaniline (12 ml) for 6 hr. The reaction mixture was worked up as usual. The separated product was crystallised from benzene as white plates, m.p. 171°, yield 1.1 g. (Found : C, 72.41, H, 5.76; $C_{13}H_{12}O_3$ requires C, 72.21, H, 5.55%). IR spectra : 31'0 cm^{-1} (-OH), 1641 cm^{-1} (>C=O).

2,9-Dimethyl-2,3-dihydro-4H-furo(3,2-f)benzopyran-4-one(Vb) :

5-Allyl-6-hydroxy-7-methylchromone (1g) was dissolved in sulphuric acid (89%, 20 ml) and the solution was heated in a water bath at 80° for 15 minutes. The contents were poured into ice cold water and extracted with ether. It was washed with dil. sodium hydroxide solution and water and the product obtained from ethereal layer was crystallised from benzene-petroleum ether as cream coloured prisms, m.p. 135°, yield 0.6 g. (Found : C, 72.07; H, 5.60; $C_{13}H_{12}O_3$ C, 72.21; H, 5.55%).;

2,9-Dimethyl-4H-furo(3,2-f) benzopyran-4-one (*VIc*) :

2,3-Dihydro-2,9-dimethyl-4H-furo(3,2-f) benzopyran-4-one (0.4 g) was refluxed in diphenyl ether (8 ml) with palladised charcoal (10%, 0.7 g) for 8 hr. The reaction mixture was worked up as described before. The dried residue was purified by elution with petroleum ether-benzene (2:3), through column pecked with sillica gel. It was crystallized from ethanol as fine small needles, m.p. 147°, yield 0.2 g. (Found : C, 72.93 ; H, 4.64 ; $C_{13}H_{10}O_3$ requires C, 72.89 ; H, 4.67%). UV λ_{max}^{MeOH} : 228 nm (log e 4·72), 264 nm (log e 4.33), 296 nm (log e 4.37), 325 nm (log e 4.30) ; NMR : δ, 2.51 (s, 3H, C_2-CH_3), 2.57 (s, 3H, C_9-CH_3), 6.29 (d, 1H, J = 6Hz, C_5-H), 7.01 (s, 1H, C_3-H), 7.37 (s, 1H, C_8-H) 7.76 (d, 1H, J = 6Hz, C_6-H).

9-Methyl-4H-furo(3,2-f) benzopyran-4-one (*VId*) :

5-Allyl-6-hydroxy-7-methylchromone (0.7 g) in ethyl acetate (120 ml) and osmium tetroxide (50 mg) in water (40 ml) were vigorously stirred for 20 minutes. Potassium periodate (1.5 g) was added in small quantities (as in case of VIb). The intermediate 5 acetaldehydo product was treated with PPA (15 ml) for 3 hr at 125°, and gave VId (160 mg). It crystallized from ethanol as fine needles, m.p. 140°. (Found : C, 71.86 ; H, 4.09 ; $C_{12}H_8O_3$ requires C, 72.00 ; H, 4.00%). NMR : δ, 2.62 (s, 3H, C_9-CH_3), 6.35 (d, 1H, J = 6Hz, C_5-H), 7.28 (d, 1H, J=2Hz, C_3-H) 7.78-7.89 (m, 3H, C_2-H, C_6-H and C_8-H).

Acknowledgement

The thanks are due to Dr. Sukh Dev, Director Maltichem. Research Centre, Nandesari, Baroda for NMR Spectra, Prof. E. Gellert, Wollongong University, Wollongong, Australia, for IR Spectra, Dr. S. S. Lele and Shri S. S. Madhava Rao for the micro analysis of the compounds, and the U. G. C., New Delhi for the award of a research fellowship to one of us (R. J. P).

References

1. K. P. Sanghvi and K. N. Trivedi, *J. Indian Chem. Soc.*, 1978, 55, 468.
2. W. Baker and O.M. Lothian, *J. Chem. Soc.*, 1935, 628 ; 1936, 274.

J. Indian Chem. Soc.,
Vol. LVII, May 1980, pp. 536-538

Studies in the Synthesis of Quinoline Derivatives. Part IX[1] : Synthesis of Pyrano (3,2-c) Quinolines

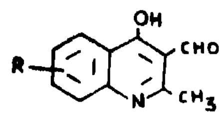
P. V. THAKORE and K. N. TRIVEDI

Chemistry Department, Faculty of Science, M. S. University of Baroda, Baroda-390 002

Manuscript received 23 August 1979, accepted 4 March 1980

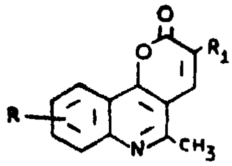
2-Methyl-3-formyl-4-hydroxyquinoline derivatives (I), on Perkin reaction with acetylglycine, acetic anhydride and triethylamine gave 3-acetamido-5-methyl-2-oxo-2H-pyrano (3, 2-c) quinoline derivatives(IIa) which on hydrolysis with dil. H_2SO_4 (50%) gave 3-hydroxy-5-methyl-2-oxo-2H pyrano (3, 2-c) quinoline derivatives (IIb). (I), on Knoevenagel condensation with diethyl malonate, ethyl acetoacetate and ethyl cyanoacetate, gave (III a), (III b) and (III c) respectively.

In continuation of our work on the synthesis of pyrano quinolines[1], we report here the synthesis of 2-oxo-2H-pyrano (3, 2-c) quinoline derivatives. 2-Methyl-3-formyl-4-hydroxy quinoline derivatives (I) on Perkin reaction with acetylglycine, acetic anhydride and triethylamine gave 3-acetamido-5-methyl-2-oxo-2H-pyrano (3, 2-c) quinoline (II a). I. R. spectrum of (II a) showed stretching bands at 1740 cm^{-1} (lactonyl >C=O group) and 16·0 cm^{-1} (amide >C=O group). (II a), on hydrolysis with dilute H_2SO_4 (50%) in ethyl alcohol in nitrogen atmosphere gave 3-hydroxy-5-methyl-2-oxo-2H-pyrano (3, 2-c) quinoline (II b). (II b) developed a green colouration with alcoholic ferric chloride solution which is characteristic of 3-hydroxy coumarin derivatives. I. R. spectrum of (II b) showed bands at 3300 cm^{-1} (broad, OH group) and 1730 cm^{-1} (lactonyl > C=O group).



(I)

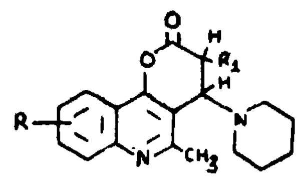
(Ia) R=H
(Ib) R=8-Me
(Ic) R=6-Me
(Id) R=6-MeO
(Ie) R=6-EtO



(II)

(IIa) R=H, R_1=–NH–CO–CH_3
(IIb) R=H, R_1=–OH
(IIc) R=H, R_1=–CO–CH_3

2, 8-Dimethyl-3-formyl-4-hydroxyquinoline, 2, 6-dimethyl-3-formyl-4-hydroxy quinoline, 2-methyl-3-formyl-4-hydroxy-6-methoxy quinoline and 2-methyl-3-formyl-4-hydroxy-6-ethoxy quinoline on similar series of reactions gave the corresponding 3-hydroxy-pyrano-(3, 2-c) quinoline derivatives.



(III)

(IIIa) R=H, R_1=–$COCH_3$
(IIIb) R=H, R_1=–$COOC_2H_5$
(IIIc) R=H, R_1=–CN

(I), on Knoevenagel condensation with ethyl acetoacetate in the presence of pyridine-piperidine mixture, gave a novel compound 3-acetyl-4-(N-piperidyl)-3, 4-dihydro-2-oxo-2H-pyrano (3, 2-c) quinoline (III a) and not the normal product (II c). The I. R. spectrum of (III a) showed bands at 1730 cm^{-1} (lactonyl > C=O group), 1640 cm^{-1} (–$COCH_3$ group). The structure of (III a) was confirmed by NMR spectrum (CF_3COOH) : δ ; 1.88, broad singlet, 6H, -CH_2- group at $C_{3'}$, 4', 5' of piperidine ; 2.25, singlet, 3H, -CH_3 group at C_5 ; 3.33, broad singlet, 4H, -CH_2- group at $C_{2'}$, 6' of piperidine ; 3.7, doublet, J=6Hz, 1H at C_4 ; 4.1 doublet, J=6Hz, 1H at C_3 and 8.1–8.6, multiplet, 4H, aromatic. The structure of (III a) was further supported by mass-spectrum which did not show the molecular ion peak, but the following peaks were prominent ; m/e ; 254, (M – piperidyl group), 226, (M ± piperidyl – CO group), 84, ($C_5H_{10}N^+$).

When (I), was condensed with diethyl malonate as above, it gave 3-carbethoxy-4-(N-piperidyl)-3, 4-dihydro-

5-methyl-2-oxo-2H-pyrano (3, 2-c) quinoline (III b). The structure of (III b) was confirmed by its IR and NMR spectra. The IR spectrum of (III b) showed bands at 1700 cm^{-1} (lactonyl > C=O group) and 1640 cm^{-1} for > C=O of carbethoxy group. The NMR (CF_3COOH) showed signals at δ; 1.55, triplet, J=8H$_z$, 3H-CH_3 group of ester ; 1.80, (broad singlet, 6H, -CH_2-groups $C_{3'}$, 4', 5' of piperidine ; 2.25, singlet, 3H, -CH_3 group at C_5, 3.65, doublet, J=6H$_z$, 1H at C_4 ; 4.00, double J=6H$_z$, 1H at C_3, 3.35, broad singlet, 4H, -CH_2-group at $C_{2'}$, 6' of piperidine ; 4.6 quartet, J=8 H$_z$, 2H, -CH_2-group of ester and 8.2 – 8.8 multiplet, 4H, aromatic.

(I), on similar condensation with ethyl cyanoacetate gave, 3-cyano-4-(N-piperidyl)-3, 4-dihydro-5-methyl-2-oxo-2H pyrano (3, 2-c) quinoline (III c).

It appears that (I) on Knoevenagel condensation with ethyl acetoacetate first forms 3 – acetyl -5-methyl-2-oxo-2H-pyrano (3, 2-c) quinoline, (II c), which reacts further to undergo Michael condensation with piperidine to give (III b).

Experimental

3-Hydroxy-5-methyl-2-oxo-2H-pyrano (3, 2-c) quinoline :

A mixture of 2-methyl-3-formyl-4-hydroxy quinoline (1.0 g) acetyl glycine (1.2 g), acetic anhydride (10.0 ml) and triethylamine (4.0 gm) was refluxed on an oil bath at 110° for 20 hrs. The reaction mixture was then poured into water and separated product was filtered and then crystallized from acetic acid ; yield (2.0 gm) m. p. 298° (Found C, 67.05 ; H, 4.35 ; N, 9.997 ; $C_{15}H_{12}N_2O_3$; requires C, 67.18 ; H, 4.48 ; N, 10.45%.). The above product (1.0 g) was heated with 50% dilute H_2SO_4 and ethyl alcohol (1 : 1) mixture (40 ml) in an inert atmosphere of N_2 gas for 5-6 hrs. The reaction mixture was diluted with water and neutralised with 10% Na_2CO_3 solution, to give free base. The separated product was filtered and washed with water. It crystallised from alcohol, yield 0.6 gm. The m. p.s and analytical data of compounds thus prepared are reported in Table 1.

3-Carbethoxy-4-(N-piperidyl)-5-methyl-3, 4-dihydro-2-oxo-2H-pyrano (3, 2-c) quinoline :

2-Methyl-3-formyl-4-hydroxy quinoline (1.0 g) was dissolved in pyridine (10 ml.) and was refluxed with diethylmalonate (1.0 ml) in the presence of few drops of piperidine on steam bath for 2 hrs. The reaction mixture was then left overnight at room temperature. The product obtained was filtered and washed with petroleum ether to remove unreacted compounds. The product crystallised from ethanol, yield 1.0 gm, m. p. 220° (d). (Found C, 68.68 ; H, 6.549 ; N, 7.39 ; $C_{21}H_{24}N_2O_4$; requires C, 68.50; H, 6.523; N, 7.61%).

The m. p.s and analytical data of these compounds prepared by condensation of 2-methyl-3-formyl-4-hydroxy quinoline derivatives, with ethylacetoacetate and ethyl cyano acetate are recorded in Table 2.

TABLE 1—5-METHYL-2-OXO-2H-PYRANO (3,2-C) QUINOLINE DERIVATIVES

R	R_1	M.P. °C	Found C%	Found H%	Found N%	Molecular formula	Required C%	Required H%	Required N%
H	$NHCOCH_3$	298	67.05	4.53	9.99	$C_{15}H_{12}N_2O_3$	67.18	4.48	10.45
H	OH	251	68.56	4.12	6.08	$C_{13}H_9NO_3$	68.70	3.96	6.17
7-methyl	$NHCOCH_3$	307	68.36	4.65	9.62	$C_{16}H_{14}N_2O_3$	68.10	4.96	9.93
7-methyl	OH	274	69.26	4.48	5.48	$C_{14}H_{11}NO_3$	69.72	4.56	5.81
9-methyl	$NHCOCH_3$	311	68.00	4.58	9.95	$C_{16}H_{14}N_2O_3$	68.10	4.96	9.93
9-methyl	OH	320	69.57	4.80	5.73	$C_{14}H_{11}NO_3$	69.72	4.56	5.81
9-ethoxy	$NHCOCH_3$	272	64.97	5.16	8.83	$C_{17}H_{16}N_2O_4$	65.38	5.12	8.97
9-ethoxy	OH	242	66.63	4.45	4.85	$C_{15}H_{13}NO_4$	66.42	4.79	5.16
9-methoxy	$NHCOCH_3$	275	63.98	4.58	8.93	$C_{16}H_{14}N_2O_4$	64.43	4.69	9.40
9-methoxy	OH	221	65.67	4.47	5.85	$C_{14}H_{11}NO_4$	65.38	4.28	5.44

TABLE 2—4-(N-PIPERIDYL)-5-METHYL-3,4-DIHYDRO-2-OXO-2H PYRANO (3,2-C) QUINOLINE DERIVATIVES

R	R_1	M.P. °C	Found C%	Found H%	Found N%	Molecular formula	Required C%	Required H%	Required N%
H	$-COOC_2H_5$	220 (dec.)	68.68	6.54	7.39	$C_{21}H_{24}N_2O_4$	68.50	6.52	7.61
H	$-COCH_3$	192 (dec.)	71.37	6.27	8.21	$C_{20}H_{22}N_2O_3$	71.00	6.51	8.28
H	$-CN$	156 (dec.)	70.52	6.01	12.58	$C_{19}H_{19}N_3O_2$	71.02	5.92	13.08
9-methyl	$-COOC_2H_5$	243	69.21	6.62	7.80	$C_{22}H_{26}N_2O_4$	69.10	6.80	7.33
9-methyl	$-COCH_3$	220 (dec.)	72.08	6.43	8.00	$C_{21}H_{24}N_2O_3$	71.60	6.82	8.07
9-methyl	$-CN$	278 (dec.)	71.99	6.69	12.05	$C_{20}H_{21}N_3O_2$	71.65	6.27	12.54
7-methyl	$-COOC_2H_5$	213	68.96	6.75	7.45	$C_{22}H_{26}N_2O_4$	69.10	6.80	7.33
7-methyl	$-CN$	178 (dec.)	71.77	6.50	12.22	$C_{20}H_{21}N_3O_2$	71.65	6.27	12.54
9-methoxy	$-COOC_2H_5$	231 (dec.)	66.87	6.32	7.19	$C_{22}H_{26}N_2O_5$	66.33	6.53	7.03
9-methoxy	$-COCH_3$	216 (dec.)	68.28	6.20	7.50	$C_{21}H_{24}N_2O_4$	68.50	6.52	7.61
9-ethoxy	$-COOC_2H_5$	188 (dec.)	67.19	6.46	7.54	$C_{23}H_{28}N_2O_5$	67.00	6.80	6.80

Acknowledgement

The authors thank Dr. Sukh Dev, Director, Maltichem Research Center, Nandesari, Baroda, for NMR spectra; Dr. Nityanand, Director, Central Drugs Research Institute, Lucknow, for mass spectra; Dr. Natarajan, Sarabhai Research Center, Baroda for IR Spectra and Dr. S. S. Lele, M. S. University of Baroda for micro-analysis.

References

1. R. J. CHUDGAR and K.N. TRIVEDI, *J. Indian Chem. Soc.*, 1972, 49, 41.

J. Indian Chem. Soc.,
Vol. LVII, May 1980, pp. 539-541

Studies in Pyrazolone-Azo Dyes. Part II : Synthesis of Some 1-Anilinomalonyl-3-Methyl-4-Substituted Phenyl-Azo-5-Pyrazolones*

V. S. JOLLY, A. K. SHRIVASTAVA, S. P. SINGH and K. S. TIWARI

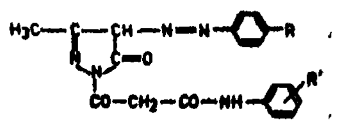
Department of Chemistry, Maharaja College, Chhatarpur-471 001

Manuscript received 20 February 1979, accepted 9 January 1980

Synthesis of some 1-anilinomalonyl-3-methyl-4-substituted phenyl-azo-5-pyrazolones is reported. Ethylacetoacetate on condensing with diazotised amines gave ethyl-α-substituted phenyl-azo-acetoacetates which on treatment with acid hydrazides of malonanilic acid series, in acetic acid, gave pyrazolone-azo dyes. These dyes impart mostly yellow colour to cotton, silk, wool and polyester fibres. None of the products show significant bacteriostatic or fungicidal activity.

In view of anticancerous, fungicidal and bacteriostatic activities of pyrazolone derivatives[1-4] and of malonanilic acid hydrazides[5] and profiting by the earlier work of Jolly and co-workers[6] we undertook the synthesis of some new pyrozolone-azo dyes having anilinomalonic acid moiety.

The experimental conditions leading to these dyes comprised condensation of ethylacetoacetate with diazotised aromatic amines affording ethyl-α-(substituted) phenyl-azo-acetoacetates. The later on heating with acid hydrazides of malonanilic acid series furnished pyrozolone-azo-dyes of the type I.



I, R=CH_3 or CO_2H or NO_2

Data concerning the dyes are set out in the Table 1. Most of the dyes are yellow in colour and possess high melting point. The IR spectra of the pyrozolone-azo-dyes showed the presence of N=N, C=N and C=O bonds as sharp and strong peaks in the region, 1570-1540 cm^{-1}, 1600-1585 cm^{-1} and 1675-1660 cm^{-1} respectively. Some of the dyes (Sl. No. 1, 4, 6, 10, 14, 17, 18, 20, 24, 25, 28, 31, 33 and 35, Table 1), have been examined for their dyeing characteristics on cotton, silk, wool and polyester fibres. These dyes produced mostly yellow shades on these fibres.

Biological activity : The compounds (Sl. No. 1, 14, 17, 28, 31 and 33, Table 1) have been tested for antimicrobial activity against *S. typhi*, *E. coli*, *C. albicans*, *C. neoformelus*, *T. mentagrophytes*, *M. canis* and *A. mgei*, at concentration 100 $\mu g/ml$. All of them were found to be ineffective.

Experimental

Ethyl-α-(substituted) phenyl-azo-acetoacetate[4] and malonanilic acid hydrazides[5] were prepared by the methods reported in the literature.

Preparation of 1-anilino-malonyl-3-methyl-4-p-methyl-phenyl-azo-5-pyrazolone :

Ethyl-α-*p*-methyl phenyl-azo-acetoacetate (0.49 g) and malonanilic acid hydrazide (0.38 g) were dissolved in acetic acid (6.5 ml) and the mixture was refluxed for three hours. Solution was concentrated and cooled in ice when the dye separated. It was filtered and recrystallised from aqueous acetic acid. Yield, 0.40 g (53.3%), m. p. 280°. IR(KBr) :

*Abstract No. ORG-59 ; Annual Convention of Chemists, 1978. For part I : *Indian J. Chem.*, (in press).

TABLE 1 – PHYSICAL DATA ON 1-ANILINO MALONYL-3-METHYL-4-SUBSTITUTED PHENYL AZO-5-PYRAZOLONES (I)

S. No.	R′	Colour	m. p. °C	Mol. formula	N% Found	N% Calc.
			$R=CH_3$			
1.	H	Y	280	$C_{20}H_{19}O_3N_5$	18.74	18.56
2.	$CH_3(o)$	LY	291	$C_{21}H_{21}O_3N_5$	18.01	17.90
3.	$CH_3(m)$	LY	294	$C_{21}H_{21}O_3N_5$	18.06	17.90
4.	$CH_3(p)$	DY	299	$C_{21}H_{21}O_3N_5$	17.79	17.90
5.	Cl (o)	Y	295	$C_{20}H_{18}O_3N_5Cl$	17.23	17.01
6.	Cl (m)	BY	>300	$C_{20}H_{18}O_3N_5Cl$	17.40	17.01
7.	Cl (p)	BY	308	$C_{20}H_{18}O_3N_5Cl$	17.41	17.01
8.	$OCH_3(o)$	Y	293	$C_{21}H_{21}O_4N_5$	17.22	17.19
9.	$OCH_3(m)$	Y	297	$C_{21}H_{21}O_4N_5$	17.30	17.19
10.	$OCH_3(p)$	BY	302	$C_{21}H_{21}O_4N_5$	17.28	17.19
			R=COOH			
11.	H	Y	296	$C_{20}H_{17}O_5N_5$	17.16	17.19
12.	$CH_3(o)$	BY	308	$C_{21}H_{19}O_5N_5$	16.46	16.62
13.	$CH_3(m)$	DY	>300	$C_{21}H_{19}O_5N_5$	16.45	16.62
14.	$CH_3(p)$	Y	301	$C_{21}H_{19}O_5N_5$	16.80	16.62
15.	Cl (o)	Y	286	$C_{20}H_{16}O_5N_5Cl$	15.92	15.85
16.	Cl (m)	Y	298	$C_{20}H_{16}O_5N_5Cl$	15.88	15.85
17.	Cl (p)	BY	290	$C_{20}H_{16}O_5N_5Cl$	15.86	15.85
18.	$OCH_3(o)$	BY	287	$C_{21}H_{19}O_6N_5$	16.18	16.23
19.	$OCH_3(m)$	Y	>300	$C_{21}H_{19}O_6N_5$	16.16	16.23
20.	$OCH_3(p)$	BY	306	$C_{21}H_{19}O_6N_5$	16.24	16.23
21.	$OC_2H_5(o)$	Y	284	$C_{22}H_{21}O_6N_5$	15.48	15.52
22.	$OC_2H_5(p)$	Y	292	$C_{22}H_{21}O_6N_5$	15.46	15.52
23.	COOH(o)	BY	302	$C_{21}H_{17}O_7N_5$	15.58	15.50
24.	COOH(p)	BY	312	$C_{21}H_{17}O_7N_5$	15.54	15.50
			$R=NO_2$			
25.	H	DY	266	$C_{19}H_{16}O_5N_6$	20.46	20.58
26.	$CH_3(o)$	DY	262	$C_{20}H_{18}O_5N_6$	19.80	19.90
27.	$CH_3(m)$	BY	268	$C_{20}H_{18}O_5N_6$	19.87	19.90
28.	$CH_3(p)$	DY	251	$C_{20}H_{18}O_5N_6$	19.75	19.90
29.	Cl (o)	DY	265	$C_{19}H_{15}O_5N_6Cl$	18.79	19.00
30.	Cl (m)	Y	228	$C_{19}H_{15}O_5N_6Cl$	19.08	19.00
31.	Cl (p)	DY	255	$C_{19}H_{15}O_5N_6Cl$	19.10	19.00
32.	$OCH_3(m)$	DY	264	$C_{20}H_{18}O_6N_6$	19.10	19.13
33.	$OCH_3(p)$	Y	253	$C_{20}H_{18}O_6N_6$	19.11	19.13
34.	$OC_2H_5(o)$	LY	271	$C_{21}H_{20}O_6N_6$	18.60	18.58
35.	$OC_2H_5(p)$	Y	260	$C_{21}H_{20}O_6N_6$	18.63	18.58
36.	$C_2H_5(o)$	DY	275	$C_{21}H_{20}O_5N_6$	18.57	18.42

BY=Bright Yellow, DY=Deep Yellow, LY=Light Yellow, Y=Yellow.

1565 cm^{-1} (N=N), 1595 cm^{-1} (C=N) and 1670 cm^{-1} (C=O). Found : N, 18.74 ; $C_{20}H_{19}O_{3}N_{5}$ requires N, 18.56%.

The aforementioned procedure is illustrative of the method used in the preparation of the dyes listed in the Table 1.

Acknowledgement

We express our gratitude to the Director, C. D. R. I., Lucknow for screening the compounds for biological activity and for I. R. Spectra. The junior research fellowships awarded by the C. S. I. R., New Delhi (to AKS, SPS and KST) are gratefully acknowledged.

References

1. W. Wilson and N. Bottiglieri, *Cancer chemotherapy*, 1962, 21, 137.
2. G. S. Saharia and H. R. Sharma, *J. Indian Chem. Soc.*, 1974, 51, 351.
3. P. S. Fernandes, B. Sandhya, G. Philip and V.V. Nadkarny, *J. Indian Chem. Soc.*, 1976, 53, 830.
4. K. Shrivastava and J. K. Mahrotra, *Indian J. Appl. Chem.*, 1969, 32, 116.
5. B. S. Rathore and P. I. Ittyerah, *J. Indian Chem Soc.*, 1960, 37, 591.
6. V. S. Jolly, unpublished work.

J. Indian Chem. Soc.,
Vol. LVII, May 1980, pp. 542-545

Evaluation of an Appropriate Parameter for Steric Effect**

S. C. DASH and G. B. BEHERA*

Department of Chemistry, Sambalpur University, Burla-768 017

Manuscript received 8 January 1979, accepted 9 January 1980

The observed pKa values of eight sets of substituted organic acids have been fitted to the equation, pKa = $p_i^\circ + \alpha_i f_j F_k + \beta_i r_j R_k + \delta f$ (steric), where $f_j F_k$, $r_j R_k$ and f (steric) refer to field, resonance and steric factors respectively. The values of p_i°, α_i, β_i and δ are obtained by multiple regression analysis method. From the values of multiple correlation co-efficient and t-test, it has been concluded that steric density (SD) is also an appropriate parameter for steric effect.

SWAIN and Lupton[1] proposed two position independent parameters, F and R to explain the effect of the substituents attached to the benzene ring. Williams and Norrington[2] suggested positional weighting factors, f and r, for these parameters and showed the applicability in different equilibria by using equation 1.

$$pKa = P_i^\circ + \alpha_i f_j F_k + \beta_i r_j R_k \pm e_i \qquad \ldots (1)$$

However, it is noted that the calculated values for ortho-substituted compounds deviate markedly from the observed ones due to some perturbation. No steric term was incorporated in the above equation perhaps due to Charton's[3] work that ortho substituents attached to sp^2 carbon exert only electronic effect. To explain the perturbation noted by Williams and Norrington, it was hoped that the incorporation of an appropriate steric term may explain the results better. With this background equation 2 has been written.

$$pKa = P_i^\circ + \alpha_i f_j F_k + \beta_i r_j R_k + \delta\, f(\text{steric}) \pm e_i \qquad \ldots (2)$$

In these equations, P_i° is the value of the intercept; F_k and R_k are the field and the resonance parameters respectively for different substituents; f_j and r_j are the positional weighting factors for different positions of the benzene nucleus; α_i and β_i represent the sensitivity of the reaction to the substituent dependent products $f_j F_k$ and $r_j R_k$ respectively for a given reaction series, δ is the sensitivity of the reaction to the appropriate steric function, f(steric). The different steric functions chosen for the present analysis are $\triangle V_w$, $\triangle \log V_w$ and steric density (SD) where,

$$V_w = (V_w)_{substituent} - (V_w)_H = (V_w)_k - 3.45,$$

$$\log V_w = \log(V_w)_k - \log(V_w)_H = \log(V_w)_k - 0.538$$

$$SD = (M.W/V_w)_k - (M.W/V_w)_H = (M.W/V_w)_k - 0.29$$

M.W is the molecular weight and V_w is the van der Waal's volume[4] for different substituents, k.

The following sets of data have been analysed in the present work.

Set 1 : pKa of 2-substituted phenoxyaceticacids[5] (n=9). H 3.171, F 3.085, Cl 3.051, Br 3.123, I 3.173, CN 2.975, NO_2 2.896, CH_3 3.227, OCH_3 3.231.

Set 2 : pKa of 2-substituted benzoicacids[6] F 3.267, Cl 2.9215, Br 2.854, I 2.863, Me 3.9083, Et 3.793, OMe 4.094, Ph 3.46, H 4.203, NO_2 2.173.

Set 3 : pKa of 2-substituted paraaminobenzoicacids[7] H 4.67, F 4.13, Cl 3.88, Br 3.69, I 3.81, OH 3.52, NO_2 2.78, NH_2 5.81, OMe 5.04, OEt 5.09, OC_3H_7 4.96, OC_4H_9 5.25, CH_3 4.83, OC_5H_{11} 5.1.

Set 4 : pKa of substituted thiophene-2-carboxylicacids[8] H 3.51, *o*-OMe 4.25, *o*-Me 3.9, *o*-SMe 3.86, *o*-Br 3.24, *o*-SOMe 2.92, *o*-SO_2Me 2.56, *m*-Br 3.15, *m*-NO_2 2.8, *p*-OMe 3.78, *p*-Me 3.74, *p*-SMe 3.51, *p*-Br 3.27, *p*-SO_2Me 2.81, *p*-Cl 3.3 ; *p*-NO_2 2.78, *m*-Me 3.58.

Set 5 : pKa of cinnamicacids[5] H 4.438, *o*-Cl 4.234, *o*-NO_2 4.151, *o*-OH 4.613, *o*-Me 4.5, *o*-OMe 4.46, *m*-Cl 4.293, *m*-NO_2 4.12, *m*-OH 4.397, *m*-Me 4.42, *m*-OMe 4.376, *p*-Cl 4.413, *p*-NO_2 4.046, *p*-Me 4.564, *p*-OMe 4.54.

Set 6 : pKa of phenylaceticacids[5] H 4.312, *o*-Cl 4.068, *o*-Br 4.053, *o*-I 4.038, *o*-NO_2 4.004, *m*-Cl 4.14, *m*-I 4.159, *m*-NO_2 3.967, *p*-Et 4.373, *p*-C_3H_7(i) 4.391, *p*-Bu(t) 4.417, *p*-F 4.246, *p*-Cl 4.19, *p*-Br 4.188, *p*-I 4.178, *p*-NO_2 3.851, *p*-Me 4.37, *p*-OMe 4.36.

** This paper was presented at the Annual Convention of Chemists, 1978 held at Waltair.

et 7 : pKa of β-phenylpropionicacids[9] *o*-Me 4.6675, *m*-Me 4.6778, *p*-Me 4.684, *o*-OMe 4.8041, *m*-OMe 4.6536, *p*-OMe 4.69, *o*-Cl 4.5768, *m*-Cl 4.585, *p*-Cl 4.6073, *o*-NO_2 4.5045, *p*-NO_2 4 4737, H 4.6596.

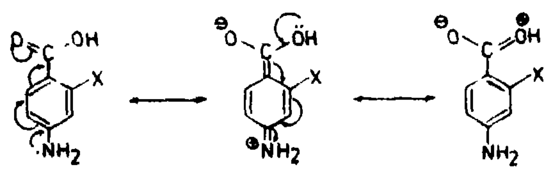
et 8 : pKa of phenylpropiolicacids in 35% dioxan[10] H 3.24, *o*-Cl 3.08. *o*-NO_2 2.83, *o*-OMe 3.37, *m*-Cl 3.00, *m*-NO_2 2.73, *m*-OMe 3.21, *p*-Cl 3.07, *p*-NO_2 2.57, *p*-OMe 3.44.

esults and Discussion

The squarred correlations (r^2) between different arameters and pKa have been calculated and given in 'able 1. The values of P_i^0, α_i, β_i, δ, multiple corre-ation co-efficient (R), standard errors (s) and F-test re evaluated by usual statistical methods and given in 'able 2.

The results in Table 1 reveal that there is a greater legree of collinearity between the pKa and the field ffect values compared to other effects.

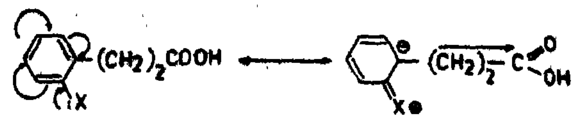
A comparison of field and resonance effects among sets indicate an order 3>2>4>8>6>5>1>7 for eld effect and 2>3>4>8>5>6>1>7 for resonance ffect. The order is same except a reversal between ets 5, 6 and 2, 3 is noted. The reversal in the sensi-ivity values between sets 2 and 3 is due to a substantial ontribution of the resonating structures involving -amino group. Obviously the demand on 'X' decreases



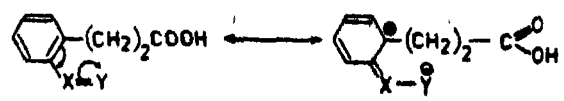
(I)

n paraaminobenzoicacids compared to 2-substituted enzoicacids. In the sets 5 and 6, presence of a double ond in set 5 increases the sensitivity to the resonance ontribution of the substituent. Hence a reversal in he order between sets 5 and 6 is noted.

The sensitivity of the pKa values to resonance and teric effect for 2-substituted phenoxyaceticacids (set 1) nd substituted beta-phenylpropioniacids (set 7) are lmost equal. The sensitivity to resonance contribution is about 0.27 to 0.28. In view of the fact that no resonance interaction is possible with the substituents and reaction site, this value appears significant. The nature of the substituent makes the aryl group an electron repelling (II) or an attracting one (III).



(II)



(III)

TABLE 1—SQUARRED CORRELATIONS OF THE VARIABLES FOR DIFFERENT SETS

				f(steric)		
		f_jF_k	r_jR_k	V_w	log V_w	SD
Set 1	pKa	0.65	0.487	0.014	0.004	0.061
	f_jF_k	1.0	0.076	0.074	0.17	0.365
	r_jR_k		1.0	0.065	0.013	0.0002
Set 2	pKa	0.761	0.153	0.004	0.054	0.379
	f_jF_k	1.0	0.003	0.042	0.0005	0.39
	r_jR_k		1.0	0.012	0.0003	0.03
Set 3	pKa	0.609	0.385	0.155	0.047	0.283
	f_jF_k	1.0	0.118	0.0002	0.023	0.365
	r_jR_k		1.0	0.148	0.206	0.026
Set 4	pKa	0.608	0.43	0.032	0.0007	0.006
	f_jF_k	1.0	0.144	0.119	0.064	0.069
	r_jR_k		1.0	0.255	0.108	0.041
Set 5	pKa	0.588	0.59	0.004	0.012	0.002
	f_jF_k	1.0	0.092	0.055	0.047	0.154
	r_jR_k		1.0	0.004	0.08	0.043
Set 6	pKa	0.837	0.305	0.223	0.228	0.173
	f_jF_k	1.0	0.105	0.244	0.252	0.152
	r_jR_k		1.0	0.019	0.019	0.002
Set 7	pKa	0.502	0.612	0.009	0.005	0.027
	f_jF_k	1.0	0.107	0.075	0.092	0.262
	r_jR_k		1.0	0 004	0.004	0.003
Set 8	pKa	0 633	0.763	0.01	0.01	0.00001
	f_jF_k	1.0	0.305	0.123	0.124	0.179
	r_jR_k		1.0	0.012	0.012	0.0002

TABLE 2—SUMMARY OF STATISTICAL DATA FOR REGRESSION ANALYSIS WITH EQUATION (2).

Set	f(Steric)	P^o_i	α_i	β_i	δ	R^a	F^b	S^c_{est}	S^c_α	S^c_β	S^c_δ	n^d	C.L.^{e} %
1	ΔV_w	3.162	−0.177	−0.266	0.0042	0.964	21.8	0.038	0.032	0.08	0.0027	9	99
	$\Delta \log V_w$	3.153	−0.181	−0.28	0.092	0.962	20.66	0.039	0.034	0.079	0.064	9	99
	SD	3.171	−0.199	−0.284	0.017	0.968	24.8	0.036	0.036	0.072	0.009	9	99
	nil	3.181	−0.159	−0.31	—	0.946	—	0.043				9	
2	ΔV_w	3.96	−1.156	−1.375	−0.012	0.961	23.89	0.223	0.149	0.492	0.006	10	99
	$\Delta \log V_w$	4.067	−1.104	−1.465	−0.511	0.969	30.96	0.198	0.129	0.433	0.211	10	99
	SD	3.809	−0.891	−1.713	−0.097	0.957	21.83	0.232	0.199	0.528	0.06	10	99
	nil	3.748	−1.097	−1.486	—	0.938		0.257				10	
3	ΔV_w	4.73	−1.46	−1.023	0.0157	0.908	15.68	0.401	0.301	0.593	0.0075	14	99
	$\Delta \log V_w$	4.659	−1.497	−1.108	0.489	0.881	11.5	0.454	0.362	0.73	0.46	14	99
	SD	4.833	−1.192	−1.557	−0.072	0.872	10.54	0.47	0.432	0.634	0.113	14	99
	nil	4.792	−1.355	−1.532		0.866		0.457				14	
4	ΔV_w	3.676	−0.748	−0.895	0.0147	0.92	23.77	0.207	0.131	0.204	0.005	17	99
	$\Delta \log V_w$	3.655	−0.736	−0.808	0.412	0.931	28.01	0.193	0.121	0.178	0.128	17	99
	SD	3.671	−0.764	−0.725	0.202	0.936	30.54	0.186	0.118	0.167	0.058	17	99
	nil	3.739	−0.68	−0.659		0.872		0.249				17	
5	ΔV_w	4.418	−0.223	−0.467	0.001	0.952	35.39	0.058	0.038	0.078	0.003	15	99.9
	$\Delta \log V_w$	4.419	−0.229	−0.446	0.044	0.954	37.38	0.057	0.037	0.081	0.053	15	99.9
	SD	4.422	−0.235	−0.447	0.014	0.954	37.2	0.057	0.04	0.081	0.017	15	99.9
	nil	4.42	−0.219	−0.471		0.951		0.058				15	
6	ΔV_w	4.317	−0.289	−0.31	−0.001	0.955	47.85	0.054	0.034	0.091	0.003	18	99.9
	$\Delta \log V_w$	4.317	−0.289	−0.31	−0.02	0.954	47.8	0.054	0.035	0.091	0.054	18	99.9
	SD	4.316	−0.28	−0.319	−0.01	0.958	52.63	0.052	0.032	0.087	0.008	18	99.9
	nil	4.318	−0.295	−0.309		0.954		0.053				18	
7	ΔV_w	4.639	−0.107	−0.267	0.003	0.941	20.48	0.035	0.025	0.059	0.002	12	99
	$\Delta \log V_w$	4.639	−0.108	−0.267	0.061	0.939	19.84	0.036	0.025	0.06	0.037	12	99
	SD	4.643	−0.112	−0.274	0.015	0.93	16.98	0.038	0.03	0.064	0.013	12	99
	nil	4.643	−0.094	−0.[illegible]85		0.917		0.039				12	
8	ΔV_w	3.231	−0.411	−0.652	0.012	0.976	40.1	0.074	0.083	0.146	0.005	10	99.9
	$\Delta \log V_w$	3.231	−0.411	−0.652	0.23	0.976	40.46	0.074	0.084	0.146	0.092	10	99.9
	SD	3.23	−0.418	−0.685	0.068	0.979	46.97	0.069	0.078	0.131	0.024	10	99.9
	nil	3.185	−0.308	−0.794		0.951		0.098				10	

a—Multiple correlation co-efficient;
b—F-test for significance of regression;
c—Standard errors of the estimate, α_i, β_i and δ;
d—Number of points in the set; and
e—Confidence level of regression.

This difference in behaviour is due to the resonance interaction of the substituent. Hence the sensitivity appears significant.

In all sets the value of multiple correlation coefficient increases with the introduction of a steric parameter. The confidence with which all the three parameters need to be used is also more than 99% (Table 2).

Acknowledgement

The authors are thankful to the University Grants Commission, New Delhi for the award of teacher fellowship to one of them (SCD).

References

1. C. G. SWAIN and E. C. LUPTON, *J. Amer. Chem. Soc.*, 1968, **90**, 4328.
2. S. G. WILLIAMS and F. E. NORRINGTON, *J. Amer. Chem. Soc.*, 1976, **98**, 508.
3. M. CHARTON, *J. Amer. Chem. Soc.*, 1969, **91**, 6649.
4. A. BONDI, *J. Phys. Chem.*, 1964, **68**, 441.
5. A. ALBERT and E. P. SERGEANT, "Ionization constants of Acids and Bases", Methuen, New York, 1962.
6. G. KORTUM, W. VOGEL and K. ANDRUSSOW, *Pure Appl. Chem.*, 1961, **1**, 190.
7. J. K. SEYDEL and W. BUTTE, *J. Med. Chem.*, 1977, **20**, 440.
8. D. SPINNELLI, R. NOTO and G. CONSIGLO, *J. Chem. Soc. (Perkin II)*, 1976, 748.
9. J. FREDERICK, J. DIPPY and J. E. PAGE, *J. Chem. Soc.*, 1938, 357.
10. MELVIN S. NEWMAN and STEWART H. MERRIL, *J. Amer. Chem. Soc.*, 1955, **77**, 5552.

Notes

Formation Constants of Transition Metal Complexes of Salicylidene-2-Iminopyridine**

G. P. SENGUPTA* and C. R. BERA

Department of Chemistry, Visva-Bharati University, Santiniketan-731 235, India

Manuscript received 4 April 1979, revised 10 October 1979, accepted 4 March 1980

SCHIFF bases derived from the reaction of aromatic aldehydes with aliphatic or aromatic amines represent an important series of widely studied ligands[1-4]. The present communication describes the results of potentiometric studies on copper (II), nickel (II) and cobalt (II) chelates of the Schiff-base ligand, salicylidene-2-iminopyridine in aqueous-ethanol medium.

Experimental

All chemicals and reagents used in the study were of A. R. Grade or purified before use.

(a) *Preparation of the ligand*: The Schiff-base ligand was prepared by taking stoichiometric amounts of salicylaldehyde and 2-aminopyridine in absolute alcohol. The mixture was heated under reflux on a water-bath when shining yellow coloured crystals appeared. It was repeatedly recrystallised in alcohol. The purity of the ligand was checked by elemental analysis and melting point determination.

(b) *Solution*: Lime distilled absolute alcohol and carbonate free sodium hydroxide solution were prepared[5]. Nitric acid (0.1M) and potassium nitrate solution were prepared in double distilled water. The ligand (0.04M) solution was made in absolute alcohol and solutions of the metal nitrates (0.01M) were done in 0.1M HNO_3. Estimation of the metal ions was made by the EDTA method[6].

(c) *Apparatus*: A digital pH-meter of Electronics Corporation of India, Model No. PH :651 (accuracy ± 0.01 units) with combined glass electrode assembly was used for the present study. All the computation works were carried out in a programmable calculator (EC 62p).

(d) *Titration*: Bjerrum-Calvin[7,8] pH-titration technique as adopted by Irving and Rossotti[9] was followed to determine the metal-ligand stability constants.

Following sets of titrations were performed at a constant temperature of 30±0.1°:

(i) 10 ml 0.1M HNO_3 + 5 ml 1M KNO_3 + 10 ml water + 25 ml absolute alcohol.

(ii) 10 ml 0.1M HNO_3 + 5 ml 1M KNO_3 + 5 ml 0.04M ligand solution + 10 ml water + 20 ml alcohol.

(iii) 5 ml 0.1M HNO_3 + 5 ml 1M KNO_3 + 5 ml 0.04M ligand solution + 5 ml 0.01M metal solution + 10 ml water + 20 ml alcohol.

The total volume in each case was 50 ml and the ionic strength was maintained constant at 0.1M KNO_3. The ratio of metal salt to reagent was maintained at nearly 1 : 4 in all titrations in order to satisfy the maximum coordination possibility of the metal ions.

Results and Discussion

In the ligand, the chelated phenolic – OH group takes part in the complex formation and the proton is replaced from it by the metal ions during complexation. Since only one proton is liberated during complexation the number of dissociable protons per ligand, (y) was taken as one.

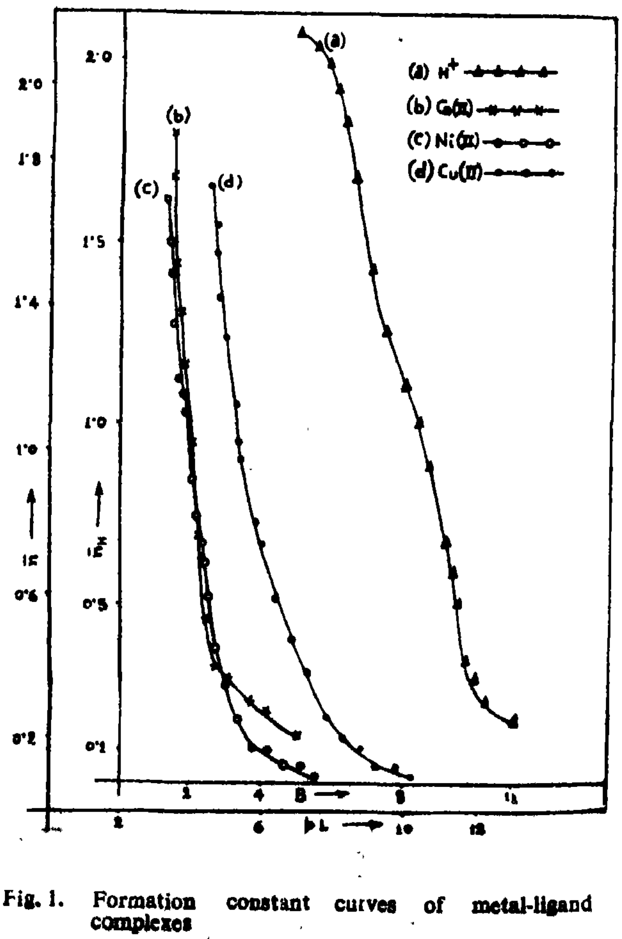


Fig. 1. Formation constant curves of metal-ligand complexes

** Paper presented in the Annual Convention of Chemists held at Waltair, 1978.

From the titration curves using solutions (i) and (ii) $\bar{n}_H$ was calculated and plotted against B-values (*p*H-meter readings) Fig. 1 (a). The values for the 'practical' proton-ligand stability constants $\log {}^{P}K_1^H$ and $\log {}^{P}K_2^H$ were evaluted by using (i) Bjerrum's half integral method and (ii) pointwise calculation method[10]. The values agree closely.

From the titration curves of the solutions (ii) and (iii) $\bar{n}$ and pL values were calculated. The $\bar{n}$ values were plotted against the corresponding pL values to get the formation curves of the metal complexation equilibria [Fig. 1 (b), (c), (d)]. The values of metal-ligand stability constants $\log k_1$ and $\log k_2$ along with the standard deviation values were determined by using the following methods : (i) Half-integral method, (ii) Schroder's method[11], (iii) Numerical method[12], (iv) Pointwise calculation[10], (v) Least square method[13] and (vi) Correction-term method[13]. In this connection it may be mentioned that Pollard *et al*[14] have made a similar study with this ligand in different mediums and under different experimental conditions and the relative magnitude of their values are nearly similar to those obtained by us. The values obtained have been given in Table1.

dimine Schiff base ligands coordinate through the azomethine nitrogen and the phenolic-OH. The azomethine nitrogen of salicylidene-2-iminopyridine shows little proton affinity while the corresponding value in case of N-phenyl salicylaldimine is relatively significant ($pK_{NH^+}=3.75$) thus indicating that the azomethine nitrogen in N-phenyl salicylaldimine is more basic compared to that in salicylidene-2-iminopyridine. The pK_{OH} value of N-phenyl salicylaldimine is also higher (9.7) than that of the present ligand. The pyridine nitrogen of salicylidene-2-iminopyridine which shows a high proton affinity ($pK_{NH^+}=5.85$)[16] does not take part in metal bonding. This has also been shown by the infra-red spectral study of the solid complexes of a similar ligand, salicylidene-2-imino-5 methyl pyridine[17], which suggest that the pyridine nitrogen is not involved in coordination and that coordination takes place through -C=N- and phenolic-OH only.

The order of $\log k_1$ values of the bivalent metal chelates was

$$Cu^{+2} > Ni^{+2} > Co^{+2}$$

This follows the Irving-Williams order[18]. Parallelisms have been observed between $\log k_1$ and second ionization potential values, on the one hand, and the atomic number of the metals, on the other.

TABLE 1—STABILITY CONSTANTS OF SALICYLIDENE-2-IMINOPYRIDINE COMPLEXES IN 50% (V/V) ETHANOL-WATER MEDIUM
TEMP.=30°C±0.1°C ; μ=0.1*M* KNO_3

Method used	(H+) $\log {}^{P}k_1^H$	(H+) $\log {}^{P}k_2^H$	(H+) $\log \beta_2$	Cu(II) $\log k_1$	Cu(II) $\log k_2$	Cu(II) $\log \beta_2$	Cu(II) δ	Ni(II) $\log k_1$	Ni(II) $\log k_2$	Ni(II) $\log \beta_2$	Ni(II) δ	Co(II) $\log k_1$	Co(II) $\log k_2$	Co(II) $\log \beta_2$	Co(II) δ
(a)	9.13	6.57	15.70	6.60	4.59	11.19	0.11	4.61	3.40	8.01	0.07	4.45	3.50	7.95	0.12
(b)	9.13	6.58	15.71	6.70	4.60	11.30	0.11	4.83	3.36	8.19	0.09	4.60	3.45	8.05	0.13
(c)				6.66	4.47	11.13	0.12	4.67	3.26	7.93	0.07	4.62	3.41	8.04	0.15
(d)				6.59	4.60	11.19	0.11	4.49	3.52	8.01	0.09	4.27	3.70	8.07	0.13
(e)				6.60	4.60	11.20	0.11	4.53	3.49	8.02	0.08	4.30	3.71	8.01	0.12
(f)				6.42	4.58	11.00	0.10	4.63	3.57	8.20	0.07	4.46	3.50	7.97	0.12
Mean Value				—	—	11.17		—	—	8.06	—	—	—	8.01	

(a)=Bjerrum Half $\bar{n}$ method ; (b)=Pointwise Calculation ; (c)=Least Square method ;
(d)=Schroder Method ; (e)=Numerical Method ; (f)=Correction term method.

The formation constant values of the copper complex may now be compared with the corresponding values reported earlier[16] for the salicylaldehyde and N-phenyl salicylaldimine ligands, though carried out in a different experimental condition. Compared to N-phenyl salicylaldimine, salicylaldehyde forms less stable complex with copper which has been attributed to the absence of chelate-ring stabilization in the copper-salicylaldehyde complex[15]. The log k values of the present Schiff base metal complexes are lower than those of N-phenyl salicylaldimine. The observed deviation may be due to the difference in the basicity of the chelating atoms present in the different coordinating sites of the Schiff base ligands. The salicylal-

Perusal of $\log \beta_2$ values shows that copper chelate is appreciably more stable than nickel and cobalt chelates. This may be due to the difference in preferred configuration between copper, nickel and cobalt complexes. The former might be forming a square plannar complex while the latter two might be forming tetrahedron complexes in solution with the Schiff base ligand under study.

Study of the solution spectra of the solid Schiff base complexes in chloroform, with their limitations in solubility, has revealed a broad transition (~14.92 KK) for Cu (II) complex which points to a square planar geometry[8], may be slightly distorted due to steric reasons. In case of Ni(II) chelate, a weak broad band could be identified at ~14.70 KK. One broad band, under the envelope of another intense ligand absorption band, has also been observed in the short wave length region (~23.5 KK). The spectral profile shows more or less a tetrahedral geometry for the Ni(II) complex. Cobalt (II) does not exhibit any absorption band in the visible range suggesting thereby a tetrahedral stereochemistry. The magnetic moment values of Cu (1.73 BM), Ni (3.4 BM) and Co (5.1 BM) also indicate the above stereochemistries for the Schiff base chelats, at least in solid state.

Acknowledgement

Thanks are due to the U. G. C. for the award of Junior Research Fellowship to one of the authors (C. R. B.)

References

1. R. H. Holm, G. W. Everett and A. Chakravorty, "*Progr. Inorg. Chem.*", (Ed.) F. A. Cotton, Interscience Publication, New York, 1966, Vol. 7, p. 83.
2. L. Sacconi, *Coord. Chem. Rev.*, 1966, 1, 126.
3. S. Yamada, *Coord. Chem. Rev.*, 1966, 1, 415.
4. R. L. Dutta and G. P. Sengupta, *J. Indian Chem. Soc.*, 1971, 48, 83.
5. A. I. Vogel, "Quantitative Inorganic Analysis", Longman Publication, London, 1961, p. 239.
6. G. Schwarzenbach, "Complexometric Titrations" Methuen & Co. Ltd., London, 1956, p. 60.
7. J. Bjerrum, "Metal Amine Formation in Aqueous Solution", Haase, Copenhagen, 1941.
8. M. Calvin and K. W. Wilson, *J. Amer. Chem. Soc.*, 1945, 67, 2003.
9. H. Irving and H. Rossotti, *J. Chem. Soc.*, 1954, 2904.
10. K. E. Jabalpurwala, K. A. Venkatachalam and M. B. Kabadi, *J. Inorg. Nuclear Chem.*, 1964, 26, 1011.
11. K. H. Schroder, *Acta. Chem. Scand.*, 1966, 20, 1401.
12. R. P. Block and G. H. McIntyre, *J. Amer. Chem. Soc.*, 1953, 75, 5667.
13. H. Irving and H. S. Rossotti, *J. Chem. Soc.*, 1953, 3397.
14. N. J. Geary, G. Nickless and F. H. Pollard, *Analyt. Chim. Acta*, 1962, 27, 71.
15. K. E. Jabalpurwala, K. A. Venkatachalam and M. B. Kabadi, *J. Inorg. Nuclear Chem.*, 1964, 26, 1027.
16. C. R. Bera, S. Chattopadhyay and G. P. Sengupta, *J. Indian Chem. Soc.*, 1979, 56, 416.
17. D. Ramaswamy and H. Ranganathan, *Curr. Sci.*, 1978, 47, 330.
18. H. Irving and R. J. P. Williams, *Nature*, 1948, 162, 746; *J. Chem. Soc.*, 1953, 3192.

Coordination Behaviour of a Tetra-substituted Pyrazole: Cobalt(II), Nickel(II) and Copper(II) Complexes with 3,4,5-Trimethyl-1-Nitroguanyl Pyrazole

NITYANANDA SAHA* and N. C. GAYEN

Department of Chemistry, University College of Science, Calcutta-700 009

Manuscript received 4 June 1979, revised 27 December 1979, accepted 9 February 1980

RECENTLY, a significant amount of research has centered around the transition-metal complexes of pyrazole-derived ligands[1] primarily because of the biological implications of the free ligands. As part of our programme[2] devoted to the study of the coordination behaviour of substituted pyrazoles, the present communication reports the synthesis of a hitherto unreported tetra-substituted pyrazole, namely, 3,4,5-trimethyl-1-nitroguanyl pyrazole (LH, Fig. 1) and its coordination behaviour by complexation with cobalt(II), nickel(II) and copper(II) salts; the solid metal complexes have been characterised from elemental analyses, magnetic susceptibility measurements, electronic and vibrational spectral data.

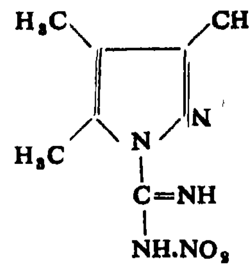


Fig. 1

Experimental

All the chemicals used were of AnalaR grade and the solvents used were purified by usual methods.

3,4,5-Trimethyl-1-nitroguanyl pyrazole (LH) was prepared by condensation of 3-methylacetylacetone[3] and nitroaminoguanidine[4] following a method similar to that adopted by R. A. Henry[5]. The product on recrystallisation from hot ethanol gave shining white crystals, m.p. 155°. The compound is soluble in hot low molecular weight alcohols, but insoluble in water. (Found: C, 42.40; H, 5.45; N, 35.80%. $C_7H_{11}N_5O_2$ requires C, 42.60; H, 5.58; N, 35.73%).

(a) $[ML_2.nH_2O]$ [n=0, M=Ni; n=2; M=Co(II), Cu(II)]: The solution obtained by mixing ethanolic solution of metalchloride hexahydrate (0.002 mole) and the ligand (0.004 mole) was adjusted to have *p*H 6 with dil. ammonia solution; the microcrystalline compound separated within few minutes (except the orange-red, NiL_2 which separated usually on heating over water-bath for 4-5 hours); in each case, this was filtered off,

washed with water and alcohol and finally dried over fused calcium chloride.

(b) $[CoL_2]$: This orange-yellow Co(II) complex was obtained by heating the hydrated variety, $CoL_2.2H_2O$ in an air-oven at 130-140° for 5-6 hours.

(c) $[CuL_2]$: To a solution of copper(II) chloride in ethanol (0.002 mole) was added a solution of the ligand (0.004 mole) in the same solvent. The resulting solution was left for 3-4 hours at room temperature. The resultant violet compound was collected as before.

The elemental analyses and other physico-chemical measurements like diffuse reflectance and i.r. spectra, magnetic susceptibilities and thermogravimetric analyses were carried out as described earlier[2].

TABLE 1—ELEMENTAL ANALYSIS AND MAGNETIC SUSCEPTIBILITY DATA OF THE METAL COMPLEXES

Complex	Colour	Found (%) Metal	Found (%) N	Calculated (%) Metal	Calculated (%) N	μ_{eff} (B.M.) at 295°K
1. $[CuL_2.2H_2O]$	Light blue	12.90	28.39	12.87	28.37	2.10
2. $[CuL_2]$	Violet	14.01	30.52	13.88	30.60	1.83
3. $[NiL_2]$	Orange red	12.98	30.84	12.96	30.92	Diamagnetic
4. $[CoL_2.2H_2O]$	Light yellow	12.17	27.66	12.07	27.60	4.60
5. $[CoL_2]$	Orange yellow	13.08	30.80	13.02	30.90	4.40

Results and Discussion

The diffuse reflectance and solution (DMF) spectra, and the effective magnetic moment values of Co(II) complexes are characteristic of a high-spin octahedral configuration. The subnormal magnetic moment values may be ascribed to spin-state equilibrium between $^4T_{1g}$ and ^2E_g states suggesting that the overall ligand field is close to the cross-over region of $3d^7$ Co(II)[6]. The abosrption bands at 8600-9600 and 19000-20400 cm^{-1} are assignable to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1) and $^4T_{1g}(F) \rightarrow {}^4T_{1g}$ (P) (ν_3) transitions respectively in an octahedral symmetry. The complex, CoL_2, has probably a polymeric octahedral structure which might be attained through bridging nitroguanyl group having additional donor sites of the ligand molecule.

The diamagnetic orange-red NiL_2 gives rise to a ligand field band at 21,740 cm^{-1} attributable to $^1A_{1g} \rightarrow {}^1A_{2g}$ (ν_2) transition characteristic of square planar Ni(II) complex[7-9]. On dissolution in pyridine, the compound does not show any spectral change which may be ascribed either to the steric interferance of the three methyl groups in the ligand or to the strong ligand-field favouring square-planar geometry[10].

The hydrated Cu(II) complex is characterised by one broad asymmetric absorption band ~15300 cm^{-1} suggesting an octahedral structure together with low symmetry components[11]. The effective magnetic moment and the mull spectrum of violet CuL_2 are diagnostic of a tetragonally distorted octahedral configuration. The main broad band at 18520 cm^{-1} and the shoulder at 15380 cm^{-1} can be assigned to $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2A_{1g}$ transitions respectively in D_{4h} symmetry[12,13]. In pyridine solution the d-d band shifts to ~14805 cm^{-1} indicating a change in stereochemistry to penta- or/hexa-coordinated species by axial interaction of solvent molecules[14-17].

In the i.r. spectra, the hydrated complexes show a medium broad band 3450 cm^{-1} attributable to ν(O-H) of attached water molecules coupled with ν(N-H)[18]. The sharp bands at 3440 and 3320 cm^{-1} in the free ligand assignable to ν_{asy} (N-H) and ν_{sy} (N-H) respectively[19] disappeared with the appearance of a new broad band around 3350-3360 cm^{-1} (the broadening of the bands may be due to the inter or intra molecular interaction) in the metal complexes thereby suggesting deprotonation of one of the N-H groups in complexation forming M-N bond[20]. The far i.r. data of NiL_2 and CoL_2 show a distinct band at 310-320 cm^{-1} region clearly assignable to M-N (ring) stretching frequency giving positive indication of the pyrazolyl nitrogen being bonded to the metal ion. The medium sharp band at ~880-885 cm^{-1} in hydrated complexes is characteristic of the rocking mode of coordinated water[18].

TGA studies indicate that the thermal stability of the complexes follows the order $NiL_2 > CuL_2 > CoL_2$. The weight-loss percentage of the hydrated complexes at 130° corresponds to the formation of anhydrous species which finally decomposes to metal oxide within 430°.

It is reasonable to conclude that the substitution of methyl group in 4-position of the pyrazole ring, being far from the coordination sites, does not exert any significant effect on the ligational behaviour of the said compound as compared to its dimethyl analogue studied earlier[2].

Acknowledgement

The authors are grateful to Professor S. E. Livingstone, Australia for kindly providing them with the reflectance spectra of the compounds.

References

1. S. TROFIMENKO, *Chem. Rev.*, 1972, 72(5), 500.
2. N. SAHA and D. BHATTACHARYYA, *Indian J. Chem.*, 1979, 18A, 154 and references therein.
3. *Organic Synthesis*, 1962, 42, 75.

4. R. PHILIPS and J. F. WILLIAMS, *J. Amer. Chem. Soc.*, 1928, 50, 2465.

5. R. A. HENRY, *J. Amer. Chem. Soc.*, 1952, 74, 278.

6. ANTONE L. TOTT II, *Inorg. Chem.*, 1974, 30, 667.

E. BANNISTER and F. A. COTTON, *J. Chem. Soc.*, 1960, 2276.

B. N. FIGGIS and R. S. NYHOLM, *J. Chem. Soc.*, 1959, 338.

7. W. MANCH and W. C. FERNELEUS, *J. Chem. Educ.*, 1961, 38, 192.

8. H. B. GRAY and C. J. BALLHAUSEN, *J. Amer. Chem. Soc.*, 1963, 85, 260.

9. W. K. MUSKER and M. S. HUSSAIN, *Inorg. Chem.*, 1969, 8, 528.

10. H. KANATOMI, I. MURASE and A. E. MARTELL, *J. Inorg. Nuclear Chem.*, 1976, 38, 1465.

11. S. C. SCHULMAN, W. P. KILROY and H. GERSHON, *J. Phys. Chem.*, 1968, 72, 3372.

12. I. M. PROCTER, B. J. HATHWAY and P. NICHOLLS, *J. Chem. Soc. (A)*, 1968, 1678.

13. K. C. PATEL and D. E. GOLDBERG, *J. Inorg. Nuclear Chem.*, 1972, 34, 637.

14. D. P. GRADDON and K. C. WATTON, *J. Inorg. Nuclear Chem.*, 1961, 21, 49.

15. H.M.N.H. IRVING and N S. ALI-MIAMI, *J. Inorg. Nuclear Chem.*, 1965, 27, 1671.

16. W. R. WAIKER and N. C. LI, *J. Inorg Nuclear Chem.*, 1965, 27, 2255.

17. W. R. MAY and M. M. JONES, *J. Inorg. Nuclear Chem.*, 1963, 25, 507.

18. K. NAKAMOTO, 'Infrared spectra of Inorganic Coordination, Compounds', John Wiley and Sons., Inc., N. Y., 1963, p. 156.

19. A. ALBERT and E. SPINNER, *J. Chem. Soc.*, 1960, 1221, 1237.

20. U. AGARWALA and L. AGARWALA, *J. Inorg. Nuclear Chem.*, 1972, 34, 251.

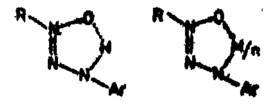
Electronic and I.R. Spectra of Some Transition Metal Complexes of Triazene-1-Oxides

R. L. DUTTA* and RAMADHAR SHARMA

Department of Chemistry, The University of Burdwan, Burdwan-713 104 (West Bengal)

Manuscript received 26 November 1979, accepted 22 December 1979

WHILE reviewing the studies done on the coordination complexes of triazene-1 oxides (TH) [I,II] we noted that the electronic and i.r. spectra of some transition metal complexes are not yet available in the literature. We report the relevant spectra of oxovanadium(IV), iron(III), cobalt(II), nickel(II) and copper(II) chelates and some mixed chelates with dipyridyl/o-phenanthroline.



(I) (II)

Results and Discussion

A. *Electronic Spectra* : (*i*) *Oxo-vanadium* (*IV*) *Complexes* [VOT_2] :

Nujol mull spectra of several substituted triazene-1-oxide complexes show two well resolved bands around 16 kK and 25 kK. According to the model proposed by Ballhausen and Gray[1] these two bands are assigned to : $d_{xy}\to d_{x^2-y^2}$ and $d_{xy}\to d_{z^2}$ transitions. Apparently the first transition $d_{xy}\to d_{xz},d_{yz}$ is not observed. Superimposable electronic spectra (Table 1) and i.r. spectra are obtained for oxovanadium(IV) complex of a given triazene-1-oxide irrespective of whether the complex is obtained from vanadyl sulphate or from ammonium vanadate. The first electronic transition gives the value of 10 Dq which is comparable to that (16 kK) observed for $[VO(H_2O)_5]^{2+}$. This indicates that the ligand field strength of the bidentate triazene-1-oxides is comparable to that of H_2O-a conclusion arrived at by Behera and Chakravorty[2] from a comparison of the electronic spectra of $[Cr(H_2O)_6]^{3+}$ (10 Dq=17.4 kK) and $[CrT_3]$ (R=alkyl, Ar=aryl) (10 Dq=17.4 kK).

TABLE 1—ELECTRONIC SPECTRA OF OXOVANADIUM(IV) COMPLEXES OF TRIAZENE-1-OXIDE

Complex	R	Ar	Electronic Spectral bands in kK	Transitions
VOT_2	C_6H_5	C_6H_5	16.0 26.6	$d_{xy}\to d_{x^2-y^2}\to d_{x^2-y^2}$ $d_{xy}\to d_{z^2}\to d_{z^2}$
VOT_2	C_6H_5	$C_6H_4.CH_3(p)$	16.1 26.0	$d_{xy}\to d_{x^2-y^2}\to d_{x^2-y^2}$ $d_{xy}\to d_{z^2}\to d_{z^2}$
VOT_2	CH_3	$C_6H_4Cl(p)$	16.1 26.6	$d_{xy}\to d_{x^2-y^2}\to d_{x^2-y^2}$ $d_{xy}\to d_{z^2}\to d_{z^2}$
VOT_2	CH_3	$C_6H_4.CH_3(p)$	16.1 26.6	$d_{xy}\to d_{x^2-y^2}\to d_{x^2-y^2}$ $d_{xy}\to d_{z^2}\to d_{z^2}$

(ii) *Mixed Chelates of Cobalt(II)* [CoT_2.*dipy/o-phen*] :

The electronic spectra of two mixed chelates of cobalt(II) containing two 1,3-diphenyl triazene-1-oxides and one dipy/o-phen were run in nujol mull as well as in acetone solution. Unfortunately only one high energy absorption band around 25 kK and one broad and weak band centered around 10.5 kK could be detected. Besides, some slight structures are observed around 16.5-18.0 kK. The low energy transition around 10 kK may be assigned to ν_1 ($^4T_{1g}\to {}^4T_{2g}$) while the second may be ν_2 ($^4T_{1g}\to {}^4A_{2g}$). Introduction of strong field

dipy/*o*-phen evidently raises the ν_1 transition compared to that of $[Co(H_2O)_6]^{2+}$ at 8.1 kK.

(iii) *Iron(III) Complexes* :

Behera[8] had reported magnetic moments (around 5.92 B.M.) and electronic spectra of three iron(III) complexes. The electronic transitions observed in benzene solutions have extremely high extinction coefficients (3200-43000), which were assigned to metal↔ligand redox transitions. Since the literature does not record any study of iron(II) complexes of these ligands, we reacted ferrous ammonium sulphate with 1,3-diphenyl triazene-1-oxide. The complex so obtained has satisfactory analyses for a formula $[FeT_3]$. The solid state spectrum of $[FeT_3]$ obtained from (a) ferrous ammonium sulphate was exactly similar to that obtained from (b) ferric ammonium sulphate. The band positions at 18.1 kK are the some as reported by Behera[8] in benzene solution. The magnetic moments of the two preparations (a) and (b) are 5.98 and 6.09 B.M. respectively. The m.p.s of the two preparations compare well with that reported by Behera (153°). We are thus convinced that ferrous iron reacts with triazene-1-oxide in air to produce ferric derivative of triazene-1-oxides.

B. *Infrared Spectra* :

The very first infrared spectrum of a triazene-1-oxide complex, namely that of oxovanadium(IV) $[VOT_2]$, was published by Dutta and Lahiry[4]. As these authors were pre-occupied with the idea of establishing the identical nature of the complex obtained from (a) vanadyl sulphate and (b) ammonium vanadate, they did no more than to present the two superimposable infrared spectra of (a) and (b). The only band they identified was that of VO at 980 cm^{-1}. In these two spectra there appeared a sharp band at around 2934 cm^{-1} which could be mistaken as ν(NH) band. Irrespective of these ligands having hydroxy triazene structure or triazene-1-oxide structure, this range should look transparent after complexation. Through over sight the authors failed to mention whether the spectra were run as KBr disc or as nujol mull. We had re-run these spectra in both KBr and nujol. In KBr no such band appears but it does so in nujol. Thus the (2934 cm^{-1}) band in the reported spectra is due to the CH stretch of nujol itself. Since no serious assignment of the different bands has so far been made either for the triazene-1-oxide ligands or their complexes, we endeavour to do so in the present communication. The

TABLE 2—IMPORTANT I.R. BANDS OF OXOVANADIUM(IV), IRON(III), COBALT(II) (HOMO AND MIXED CHELATES), NICKEL(II) AND COPPER(II) COMPLEXES OF TRIAZENE-1-OXIDES.

Compound	νN–H	νC–C (phenyl)		ν–N=N–N– (sym. triazene)		νN→O	νC–C (in plane)	νdipy/*o*-phen
1,3-diphenyl triazene-1-oxide (TH)	3160s	1600s	1510s,	1475b,	1440s	1300w	1220b	—
VOT_2	—	1600s	1482s,	1463w,	1380s	1240s	—	—
FeT_3	—	1590s	1482s,	1462w.	1375s	1235s	—	—
CoT_2	—	1590s	1480s,	1460w,	1385s	1235s	—	—
CoT_2.dipy	—	1590s	1480s,	1460w,	1370s	1240s	—	1430s,1170b,730s
CoT_2.*o*-phen	—	1590s	1480s,	1460w,	1370s	1240s	—	1425s,1170b,730s
NiT_2	—	1590s	1480s,	1460s,	1370s	1235s	—	—
CuT_2	—	1595s	1485s,	1465s,	1370s	1240s	—	—
3-*p*-tolyl-1-phenyl triazene-1-oxide (TH)	3180s	1605s	1527s,	1475b,	1430s	1305s	1215b	—
VOT_2	—	1595s	1510s,	1490w,	1465w	1245s	—	—
FeT_3	—	1595s	1510s,	1490w,	1465w	1245s	—	—
CoT_2	—	1595s	1512s,	1490w,	1462w	1245s	—	—
CoT_2.dipy	—	1595s	1510s,	1490w,	1465w	1250s	—	1430s,1170b,730s
CoT_2.*o*-phen	—	1595s	1510s,	1490w,	1465w	1245s	—	1430s,1170b,730s
NiT_2	—	1595s	1510s,	1490w,	1465w	1245s	—	—
CuT_2	—	1595s	1510s,	1490w,	1465w	1245s	—	—

s = strong ; b = broad ; w = weak.

expected i.r. bands for ν_{N-H} (3200 cm^{-1}) ν_{C-C} (phenyl ring) (1600 cm^{-1}), $\nu_{-N=N-N-}$ (sym. triazene; ($\sim$1560 – 1450 cm^{-1}) and $\nu_{N\rightarrow O}$ ($\sim$1300 – 1220 cm^{-1}) have all been located in the i.r. spectra of the triazene-1-oxide ligands[5]. $\nu_{N\rightarrow O}$ band is found to be considerably lowered ($\sim$60 cm^{-1}) due to N – O – M bond formation[6-8]. ν_{N-H} band of the ligand completely disappears in the complexes MT_2, MT_3 and MT_2 (dipy/*o*-phen) showing coordination of the metal ion through N-atom. ν_{C-C} (phenyl ring) remains almost unchanged ($\sim$10 cm^{-1}). $\nu_{-N=N-N-}$ is lowered by $\sim$26 cm^{-1} due to change in the environment of the symmetric triazene. The $\nu_{N\rightarrow O}$ (1300 cm^{-1}) is lowered to ($\sim$1240 cm^{-1}). Both in the homochelates and the mixed chelates the very sharp new band around ($\sim$1240 cm^{-1}) also covers a few weak bands as well as ν_{C-C} (phenyl in plane). Characteristic bands of coordinated dipy/*o*-phen as in [Cu(dipy)Cl_2] and [Cu(*o*-phen)Cl_2][9]; [Ni(OH_2)-Cl(dipy)$_2$]Cl2H_2O[10] around $\sim$730 cm^{-1}, $\sim$1170 cm^{-1} and $\sim$1420 cm^{-1} are observed in the spectra of [CoT_2(dipy/*o*-phen)] complexes. The important i.r. bands have been presented in Table 2.

Experimental

The chelates were prepared by following standard procedures[4,11,12]. Their characterisation data were satisfactory. Room temperature magnetic moments were measured in Gouy balance using $CuSO_4.5H_2O$ as a calibrant. The electronic spectra were run at SIC, Madras and i.r. spectra at C.D.R.I., Lucknow.

References

1. C. J. BALLHAUSEN and H. B. GRAY, *Inorg. Chem.*, 1962, 1, 111,

   C. K. JORGENSEN, *Acta. Chem. Scand.*, 1957, 11, 73.

2. B. BEHERA and A. CHAKRAVORTY, *J. Inorg. Nuclear Chem.*, 1964, 31, 1791.
3. B. BEHERA, *Indian J. Chem.*, 1972, 10, 555.
4. R. L. DUTTA and S. LAHIRY, *J. Indian Chem. Soc.*, 1963, 40, 67.
5. A. D. CROSS and R. A. JONES, An Introduction to Practical Infrared Spectroscopy, Butterworths, London (1969).
6. J. V. QUAGLIANO, J. FUJITA, G. FRANZ, D. J. PHILIPS, J. A. WALMSLEY and S. Y. TYREE, *J. Amer. Chem. Soc.*, 1961, 83, 3770.
7. A. VINCIGUERRA, P. G. SIMPSON, Y. KAKIUTI and J. V. QUAGLIANO, *Inorg. Chem.*, 1963, 2, 286.
8. R. G. GARVEY and R. O. RAGSDALE, *J. Inorg. Nuclear Chem.*, 1967, 39, 1527.
9. R. L. DUTTA and S. P. BANERJEE, *J. Indian Chem. Soc.*, 1974, 51, 497.
10. R. L. DUTTA and A. BHATTACHARYA, *J. Inorg. Nuclear Chem.* (in press).
11. M. ELKINS and L. HUNTER, *J. Chem. Soc.*, 1938, 1346.
12. R. L. DUTTA and L. DE, *J. Indian Chem. Soc.*, 1975, 52, 664.

Mixed Ligand Complexes of *bis*(ethylmalonato) Co(II), Cu(II) and Zn(II) with Nitrogen Donor Ligands

N. C. MISHRA

Chemistry Department, L. N. College, Jharsuguda

and

B. B. MOHAPATRA and SARWESHWAR GURU

Department of Chemistry, Ravenshaw College, Cuttack-753 003 (Orissa)

Manuscript received 12 June 1978, revised 27 December 1979, accepted 18 March 1980

BETA-diketones and beta-keto esters have drawn considerable attention as oxygen donorchelating ligands[1-6]. We have been trying[7,8] to prepare complexes with nitrogen donors of these metal chelates. We thought it would be worthwhile to extend our investigation to the synthesis of a number of mixed ligand complexes of Co(II), Cu(II) and Zn(II) ions with malonic ester and nitrogen donor aliphatic and heterocyclic amines.

Experimental

All the chemicals used were of AnalaR grade. The metal chelates were prepared as reported earlier[7]. Mixed ligand complexes were prepared by refluxing an ethanolic suspension of metal chelates and amines in 1:2 ratio for about two hours over water bath. On keeping the resulting solution overnight, crystalline compounds separated out which were filtered, washed with ethanol followed by ether and dried *in vacuo*. Conductance was measured in M/1000 acetone solution. Electronic spectra were recorded in M/100 chloroform solution of the complexes. All the relavant analytical and spectral data are recorded in Table 1.

Result and Discussion

All the twelve complexes reported in the present communication have the composition $[ML_2B_2]^{\circ}$, where M=Co(II), Cu(II) and Zn(II); L is malonic ester and B is either a heterocyclic or aliphatic amine. Cobalt complexes are brown, copper complexes are green and zinc complexes are white in colour and these complexes have fairly low melting points. Acetone solution of the complexes are found to be non-electrolytes as the ΔM values range between 8 to 12 mhos cm^2. The μ_{eff} values for Co(II) and Cu(II) complexes are around 5.1 and 1.8 B. M. respectively. In I. R. spectra of the mixed ligand complexes the two bands ν(C=O) at 1600 cm^{-1} and ν(C–O) at 1290 cm^{-1} are again shifted to higher frequency regions appearing around 1620 and 1310 cm^{-1} respectively indicating bonding of the σ-bonded amines to the metal ions. Moreover, most of the bands due to nitrogen bases, have been modified in the complexes which indirectly supports the bonding of the nitrogen donor ligands to metal ions. Further, the direct evidence of bonding of oxygen and nitrogen

TABLE 1 — MELTING POINT, ANALYSIS, CONDUCTANCE, MAGNETIC SUSCEPTIBILITY AND IR SPECTRAL DATA

Compound	M.P. (°C)	% Metal		% Nitrogen		Λmhos cm²	μ_{eff} (B.M.)	ν(C=O)	ν(C–O)	ν(M–O)	ν(M–N)
		Found	Reqd.	Found	Reqd.						
$[CoL_2(\alpha\text{-pic})_2]$	178	13.55	14.05	6.35	6.69	9.00	5.1	1620	1310	510	350
$[CoL_2(\gamma\text{-pic})_2]$	191	13.51	14.05	6.62	6.69	8.50	4.9	1620	1315	510	250
$[CoL_2Q_2]$	186	12.02	12.27	5.63	5.70	12.00	5.0	1610	1310	510	340
$[CoL_2(DMA)_2]$	167	17.97	18.23	8.26	8.62	8.0	5.1	1610	1305	505	345
$[CuL_2(\alpha\text{-pic})_2]$	212	13.63	15.04	6.17	6.60	10.00	1.8	1615	1310	515	340
$[CuL_2(\gamma\text{-pic})_2]$	201	13.58	15.04	6.52	6.60	9.5	1.7	1620	1310	510	350
$[CuL_2Q_2]$	179	12.71	12.86	5.48	5.64	8.0	1.75	1625	1320	510	350
$[CuL_2(DEA)_2]$	226*	16.12	16.02	7.01	7.29	12.0	1.8	1610	1310	515	345
$[ZnL_2(\alpha\text{-pic})_2]$	249*	15.55	15.37	6.29	6.58	8.5	—	1620	1315	515	340
$[ZnL_2(\gamma\text{-pic})_2]$	259*	14.86	15.37	6.50	6.58	9.0	—	1615	1310	505	350
$[ZnL_2Q_2]$	235	13.37	13.14	5.56	5.62	10.0	—	1625	1305	510	340
$[ZnL_2(DEA)_2]$	286*	17.12	19.96	7.08	7.26	10.5	—	1620	1320	510	345

* decomposition

α-pic = α-picoline, γ-pic = γ-picoline, Q = quinoline, DMA = dimethylamine, DEA = diethylamine

atoms have been provided by the occurrence of ν(M-O) and ν(M-N) around 510 cm^{-1} and 350 cm^{-1} respectively.

In the visible electronic spectra of cobalt(II) complexes two absorption bands appear ~18.0(30) and ~8.5(20) k.K. region attributable[10] to $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ and $^4T_{1g} \rightarrow {}^4T_{2g}(F)$ transition respectively. Position of absorption bands, molar absorptivity values and magnetic moment suggest a high spin octahedral configuration for the Co(II) complexes. Copper(II) complexes show one broad absorption band ~15.0(40) k.K. region indicating probably a distorted octahedral configuration, but μ_{eff} values found for Cu(II) complexes are low for Oh symmetry. Although, three transitions are expected for such complexes due to John Teller distortion, often these transitions are observed in the form of a broad envelope, as these are very close in energy. Zinc(II) complexes are presumably octahedral on the basis of analysis, conductance and I. R. spectral data.

References

1. D. P. GRADDON and D. G. WEEDEN, *Aust. J. Chem.*, 1963, 16, 980.
2. D. P. GRADDON and D. G. WEEDEN, *Aust. J. Chem.*, 1963, 17, 607.
3. R. D. GILLARD and G. WILKINSON, *J. Chem. Soc. (A)*, 1963, 5399.
4. B. K. MOHAPATRA and D. V. RAMAN RAO, *Z. Anorg. Allg. Chem.*, 1970, 372, 332.
5. B. K. MOHAPATRA and D. V. RAMAN RAO, *Inorg. Chim. Acta*, 1970, 4, 404.
6. A. K. JENA and B. K. MOHAPATRA, *J. Indian Chem. Soc.*, 1976, 53, 474.
7. B. B. MOHAPATRA, B. K. MOHAPATRA and S. GURU, *J. Indian Chem. Soc.* (In press).
8. B. B. MOHAPATRA, B. K. MOHAPATRA and S. GURU, *J. Indian Chem. Soc.* (Communicated).
9. I. R. FERRARO, Low frequency vibration of inorganic and coordination compounds, John Wiley, New York, 1971.
10. A. B. P. LEVER, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, 1968.

Studies on Complex Compounds of Nickel(II), Palladium(II) and Copper(II) with Benzaldehyde Semicarbazone

C. B. MAHTO

Department of Chemistry, Gopalganj College, Gopalganj, Bihar

Manuscript received 18 March 1978, revised 28 April 1979, accepted 25 December 1979

THE present paper reports three complexes, namely, *bis*-benzaldehyde semicarbazone Ni(II), *bis*-benzaldehyde semicarbazone Pd(II) and *bis*-benzaldehyde semicarbazone Cu(II) of the formulae, $M(C_8H_8ON_3)_2$ where M = Ni(II), Pd(II) and Cu(II).

Materials :

Semicarbazide hydrochloride (B. D. H. Grade), $NiSO_4.6H_2O$(S.M.), $CuSO_4.5H_2O$(E.M.) and $PdCl_2$ (A.M.) were used.

Complexes :

50 cc of 1% Ni(II) solution were treated with a slight excess of 0.1% hot aqueous ligand on water bath. Immediately after that, 4 (*N*) NH_4OH was added dropwise untill the complex started to be formed. Cu(II)-complex was prepared by similar method. To 30 cc of 1% Pd(II) solution in (1:1) HCl, few cc of conc. sodium acetate solution were added and then treated in cold with a slight excess of 0.1% ligand solution in 50% acetone followed by gradual addition of 4 (*N*) NH_4OH solution. The complexes were washed with hot water containing a little NH_4OH solution and dried over fused $CaCl_2$.

Results and Discussions

The results on elemental analysis, ir, uv and magnetic measurements were reported in Table 1.

appeared with centres at 345 cm^{-1}, 335 cm^{-1} and 410 cm^{-1} in the spectra of the complexes were assigned to ν(Ni – O), ν(Pd – O) and ν(Cu – O) respectively. ν(Cu – O) at 430 cm^{-1} in *bis*-semicarbazide Cu(II) was already reported by the author[6]. Agamer[7] assigned ν(M – O) at 325-35 cm^{-1}.

U.V. Spectra :

The principal band observed at 480 mμ due to $1A_{1g} \rightarrow 1B_{1g}$ transition in Ni(II)-complex was supported by Dhadke *et al*[8]. In Pd(II) complex, band at 420-10 was assigned due to $1A_{1g} \rightarrow 1B_{1g}$ transition. These facts suggested the square planar geometry of Ni(II) and Pd(II) complexes. Detailed interpretation of square planar complex of Cu(II) seemed complicated. However, 440-380 mμ band was assigned to $2B_{1g} \rightarrow 2B_g$ transition[6].

Magnetic Measurement :

Magnetic moment measurement showed Ni(II) and Pd(II) complexes to be dimagnetic. The square planar structures involved dsp^2 hybridisation. μ_{eff} for

TABLE 1

Complexes	Colours	%M Found (Cal.)	%C Found (Cal.)	%H Found (Cal.)	%N Found (Cal.)	μeff B.M.	IR spectra, cm^{-1} ν(C=N)	ν(C—O)	ν(M—O)	ν(M – N)	uv spectra λmax,mμ
$Ni(C_8H_8ON_3)_2$	Green yellow or red	14.78 14.78	50.10 50.16	4.15 4.18	21.94 29.94	0	1435 vw	1000 b	345 b	515 b	480
$Pd(C_8H_8ON_3)_2$	Orange red	24.58 24.58	44.40 44.40	3.71 3.72	19.40 19.42	0	1430 vs	1010 s	335 w	515 vw	420-10
$Cu(C_8H_8ON_3)_2$	Green blue	15.15 15.16	49.52 49.53	4.10 4.12	21.64 21.67	1.91	1450 vs	1000 vs	410	610 ms	440-38

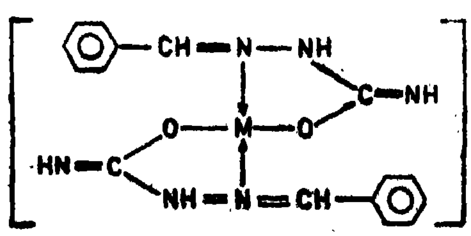
Infra Red Spectra :

I.R. spectra of the ligand and complexes were studied in nujol phase between 200 to 4000 cm^{-1} wave number. The bands at 1570-90 cm^{-1} and 1400-50 cm^{-1} in the spectra of ligand due to C=N and OH bending of enolic form of ligand decreased and modified their intensities at 1435 and 1420 cm^{-1}, 1430 and 1415 cm^{-1} and 1450 and 1465 cm^{-1} respectively in nickel-, palladium-and copper-complexes showing thus co-ordination to metal through N of C – N and also the replacement of H of enolic OH. The fact is in conformity with the observation of Saha and Bhattacharyya[1]. Rastogi and Saxena[2] reported the band due to C=N in anils at 1590-1620 cm^{-1}, while Patel and others[3] observed it at 1590-1615 cm^{-1}. The bands around 1000 cm^{-1} due to C – O as marked in the spectra of ligand and complexes, were also supported by Goel and Gupta[4]. Moreover, new bands with centres at 515 cm^{-1}, 510 cm^{-1} and 610 cm^{-1} in the spectra of complexes may be attributed to ν(Ni – N), ν(Pd – N) and ν(Cu – N) respectively. Mishra and others[5] reported bands at 500 and 510 cm^{-1} due to ν(Ni – N) and ν(Cu – N) vibrations. The bands which

Cu(II)-complex was found to be 1.91 B.M, which was greater than 1.732 B.M. This suggested it to be paramagnetic. A slight greater value was attributed due to orbital contribution and distortion of octahedral structure leading to a square planar structure.

Structures of Benzaldehyde semicarbazone complexes :

The system $-CH=\overset{1}{N}-\overset{2}{N}H-\overset{3}{C}O-\overset{4}{N}H_2$ of the ligand satisfied the condition of formation of chelates. Thus Ni(II), Pd(II) and Cu(II)-chelates can be assigned the tentative structure as follows :



References

1. N. Saha and D. Bhattacharyya, *J. Indian Chem. Soc.*, 1977, **54**, 143.
2. S. C. Rastogi and G. C. Saxena, *Acta. Ciencia. Indica.*, 1976, **2**, 103.
3. M. M. Patel, M. R. Patel and B. N. Mankad, *J. Indian Chem. Soc.*, 1976, **53**, 454.
4. A. B. Goel and V. D. Gupta, *J. Indian Chem. Soc.*, 1977, **54**, 581.
5. N. C. Mishra, B. B. Mohapatra and S. Guru, *J. Indian Chem. Soc.*, 1978, **55**, 437.
6. C. B. Mahto, *Acta. Ciencia. Indica.*, 1978, **4**, 245.
7. C. A. Agamer, P. Anstey and K. G. Orrell, *J. Chem. Soc. Dalton*, 1974, 864.
8. P. M. Dhadke and B. C. Haldar, *J. Indian Chem. Soc.*, 1979, **56**, 461.

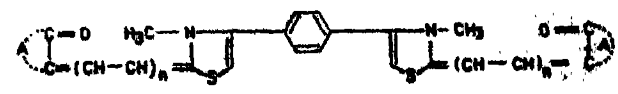
Polynuclear Photographic Sensitising Dyes Derived from 4-4′-*p*-Phenylene *Bis*-(2-Methyl Thiazole), Part-II.

P. K. JESTHI* and S. K. MOHAPATRA

Government College, Sundargarh, Orissa

Manuscript received 7 February 1979, revised 6 September 1979, accepted 9 January 1980

IN the present investigation a number of symmetrical non-ionic tetranuclear dyes (I) with two central quaternary thiazole residues, two ketomethylene residues and two (=CH−CH=)n chains derived from the diquaternary salt of 4,4′-*p*-phenylene-*bis*-(2-methyl thiazole) have been prepared. The variable acidic nuclei were derived from various ketomethylene compounds like 2-phenyl oxazolone, 2 benzylthio-thiazolone, 1-phenyl-3 methyl-pyrazolone, N,N-diphenyl-thio-barbituric acid and N-phenyl rhodanine.



(I) (A = Variable Acidic nuclei n=1, 2)

The absorption maxima of these dyes were measured. The vinylene shift for these terranuclear dyes have been found to be between 75 nm to 92 nm by comparing the absorption maxima data of the tetranuclear dyes (I, n=1) with their higher vinylene homologues (I, n=2). The vinylene shifts vary with the nature of the variable nuclei used for the preparation of these dyes.

Experimental

4-4′-*p*-Phenylene-*bis*-(2-methyl thiazole) methiodide has been prepared from 1,4-diacetyl benzene[1].

Symmetrical non-ionic tetranuclear dyes (Compound No. 1)

4-Ethoxymethylene-1-phenyl-3-methyl pyrazolone[2] (0.46g) and 4,4′-*p*-phenylene-*bis*-(2-methyl thiazole) methiodide (0.8g) were refluxed in absolute ethanol in presence of triethylamine (2-drops) for 10 minutes. The excess solvent was removed under reduced pressure. The desired product separated on cooling was recrystallised from absolute ethanol. m.p.–192° (decomp); yield. 30% (Found C, 67.85; H, 4.58; N, 12.51; S, 9.49%. $C_{38}H_{32}N_6O_2S_2$ requires C, 68.26; H, 4.64; N, 12.57; S, 9.58%).

TABLE 1—TETRANUCLEAR DYES DERIVED FROM 4,4′-*p*-PHENYLENE-*Bis*-(2-METHYLTHIAZOLE)

(Structure—I)

Sl. No.	Nature of acidic nucleus 'A'	Value of 'n'	M. P. °C	Yield %	Abs. Max in nm.	Sulphur % Found	Sulphur % Calc.	Nitrogen % Found	Nitrogen % Calc.
1.	1-methyl-3-phenyl pyrazolone	1	192 (d)	30	483	9.49	9.58	12.51	12.57
2.	-do-	2	206 (d)	25	575	8.78	8.89	11.53	11.67
3.	N-phenyl rhodanine	1	220	25	515	25.03	26.01	7.17	7.58
4.	-do-	2	206 (d)	15	606	24.50	24.61	6.84	7.18
5.	N, N-diphenyl thiobarbituric acid	1	>206	20	475	13.05	14.04	8.81	9.21
6.	-d-	2	247 (d)	25	560	13.17	13.27	8.39	8.71
7.	2-benzylthiothiazolone	1	173 (d)	15	496	24.05	25.07	6.89	7.31
8.	2-phenyl oxazol-5-one	1	>250	15	523	9.83	9.97	8.43	8.72

Other dyes were prepared by condensing the methiodide with ethoxymethylene or acetanilido methylene derivatives of other ketomethylene compounds[2].

The higher vinylene homologue of the above dye (Table 1 Compound No. 2) was obtained by the condensation of the desired methiodide (0.4g) with 4-(3-acetanilido-allylidene)-1-phenyl-3-methyl pyrazolone[2] (0.35g) in absolute ethanol in presence of triethylamine. The compound was isolated in usual manner. m.p.-206° (decomp); yield-25% (Found C, 69,48; H, 4.87; N, 11.53; S, 8·78%. $C_{42}H_{36}N_6O_2S_2$ requires C, 70.00; H, 5.00; N, 11.67; S, 8.89%). Other dyes of this type were prepared in similar manner using either acetanilido allylidene or methoxy allylidene derivatives of ketomethylene compounds[2].

The analytical data, m.p.s etc. of all these dyes are described in Table 1.

Acknowledgement

The authors are grateful to Dr. M. K. Rout, D. Sc., D.P.I. Orissa, for his interest in the work and to the Board of Scientific and Industrial Research, Orissa, for financial assistance.

References

1. P. K. JESTHI and S. K. MOHAPATRA, *Curr. Sci.*, 1972, 41, 98.
2. P. B. TRIPATHY and M. K. ROUT, *J. Sci. and Ind. Research*, 1961, 20B, 179.

Coordination Compounds of Copper(II) Derived from Schiff's bases

(Mrs.) P. R. SHUKLA and (Miss) RENU TAKROO

Chemistry Department, University of Lucknow, Lucknow

Manuscript received 15 September 1978, revised 13 December 1979, accepted 18 March 1980

THE use of aromatic Schiff's bases derived from various aldehydes and amines as either anionic monofunctional mono or multidentate or neutral mono or multidentate ligands has attracted the attention of workers in previous years[1-4]. In the present paper the interaction of aniline and toluidines with benzaldehyde in alcohol has been studied and these Schiff's bases on treatment with copper(II) salts are found to give bright green molecular compounds of 1:1 stoichiometry, whose structures have been determined on the basis of analytical and spectroscopic data.

Discussion

The electronic spectra of complexes contain three sharp bands near 235 nm, 320 nm and 680 nm. The first two of these are also seen in the spectra of free Schiff's bases and the former one corresponds to the perturbed benzene ring transition of the amine fragment and the latter to the whole aromatic molecule oriented *trans* with respect to the double bond[5,6]. The last one is the characteristic d-d transition of copper(II) in planar environment.

In the i.r. spectra of complexes one broad band appears around 3400 cm^{-1} which is absent in the spectra of free Schiff's bases. It thus shows that all complexes contain coordinated water[7,8]. The band at 1600 ± 10 cm^{-1} corresponds to the azomethine stretch, which in free ligands is observed at 1620 ± 10 cm^{-1}. This small negative shift although an indication of coordination also shows the reduced ability of the Schiff's bases to act as ligands for copper(II), due to steric reasons as already reported[9-14]. The phthalate complexes show the asymmetric and symmetric COO^- stretches at 1690 ± 10 and 1417 ± 40 cm^{-1} characteristic of co-ordinated carboxyllate ion[12]. The molar conductances of these complexes in nitrobenzene are also almost zero, as expected in view of their non electrolytic nature. The sulphate complex on the other hand behaves as 1:1 electrolyte and the ν_3 and ν_4 transitions of uncoordinated sulphate ion are seen at 1120 and 650 cm^{-1} in the i.r. spectra.

Acknowledgement

One of us (R.T.) is thankful to State Council of Science and Technology for the financial assistance, while our thanks are due to Dr. A. J. Dleming for

TABLE 1 – ANALYTICAL, MOLAR CONDUCTANCE (IN NITROBENZENE) AND MAGNETIC MOMENT DATA

Formula	% Cu	% C	% H	% N	Molar conductance in $PhNO_2$ in mhos	μeff in B. M
1. $[Cu(H_2O)_3(C_{13}H_{11}N)]SO_4$	16.51	39.72	4.52	3.62		
	(16.10)	(39.56)	(4.62)	(3.55)	20.16	1.886
2. $[Cu(H_2O)(C_{13}H_{11}N)C_8H_4O_4]$	15.01	59.43	3.88	3.22		
	(14.89)	(59.03)	(3.98)	(3.28)	0.18	1.888
3. $[Cu(H_2O)(o\text{-}C_{14}H_{13}N)C_8H_4O_4]$	14.50	59.50	4.28	3.21		
	(14.41)	(59.90)	(4.86)	(3.18)	0.13	1.888
4. $[Cu(H_2O)(m\text{-}C_{14}H_{13}N)C_8H_4O_4]$	14.62	59.82	4.72	3.35	0.08	1.884
5. $[Cu(H_2O)(p\text{-}C_{14}H_{13}N)C_8H_4O_4]$	14.75	60.02	4.50	3.50	0.07	1.882

obtaining the magnetic and electronic spectral data of the complexes.

References

1. G. S. YAMADA, *Coord. Chem. Rev.*, 1966, 4, 415.
2. T. N. WALTERS and P. E. WRIGHT, *J. Inorg. Nuclear Chem.*, 1971, 33, 359.
3. O. B. WEST "New Pathways in Inorg. Chem", 1968, 303.
4. G. R. BRUBAKER, C. J. LATTA and C. DOLORES, *Inorg. Chem.*, 1970, 9, 268.
5. V. I. MINKIN, O. A. OSIPOV, V. A. KOGAN, R. R. SHAGIDUSHEIMA, R. L. TERENTEEV and O. A. RAEVSKII, *Russ. J. Phys. Chem.*, 1964, 38, 938.
6. M. O. COHEN and S. FLAVIAN, *J. Chem. Soc.*, 1967, 321.
7. K. VENO and A. E. MARTELL, *J. Phys. Chem.*, 1955, 59, 998.
8. A. E. MARTELL, R. L. BELFORD and M. COLVIN, *J. Inorg. Nuclear Chem.*, 1958, 5, 170.
9. A. S. EGOROV, V. A. KOGAN, O A. OSIPOV and I. G. STRIZHKOVA, *Russ. J. Inorg. Chem.*, 1975, 20, 365.
10. R. N. PRASAD and J. P. TANDON, *J. Less Common Metals*, 1974, 37, 141.
11. S. K. AGARWAL and J. P. TANDON, *Syn. React. Inorg. Metal-Org. Chem.*, 1974, 4, 387.
12. S. F. A. KETTLE and A. J. P. PIOLE, *J. Chem. Soc. (A)*, 1966, 1423.

Structural Studies on Palladium(II) and Cobalt(III) Complexes of Isonitroso-β-diketones

B. J. DESAI and V. M. SHINDE*

Department of Chemistry, Shivaji University, Kolhapur-416 004, India.

Manuscript received 16 April 1979, revised 21 August 1979, accepted 4 March 1980

ISONITROSOBENZOYLACETONE (HINBA) and isonitrosodibenzoylmethane (HINDBM) have been used in this laboratory for the spectrophotometric determination of iron, palladium and ruthenium[1-3]. The present communication deals with the preparation and structural characterization of solid complexes of Pd(II) and Co(III) with HINBA and HINDBM.

Experimental

All chemicals used were of AnalaR grade. HINBA and HINDBM were prepared by the reported methods[4]. Palladium complexes were prepared by mixing acidic solution of $PdCl_2$ and alcoholic solution of ligand in 1:2 molar ratio. On dropwise addition of sodium acetate orange-red complexes precipitates out. The precipitate was digested on a hot plate for 20-30 min, filtered, washed with water, ethanol and finally dried under vacuum. Cobalt(III) complexes were prepared by mixing aqueous solution of $CoCl_2$ and alcoholic solution of ligand in 1:3 molar ratio and then added sodium hydroxide solution to precipitate complexes. Rest procedure is followed as above.

Metal was estimated by standard methods and nitrogen by microanalytical method. Magnetic susceptibility measurement was made by Gouy method using $Hg[Co(NCS)_4]$ as calibrant. IR spectra were recorded on NaCl(KBr) prism using Perkin-Elmer (221) Spectrophotometer. Electronic spectra were recorded using Beckman DU-2 spectrophotometer and PMR were recorded in $CDCl_3$ using varian spectrometers with TMS as the standard. The molecular weights of the complexes were determined by cryoscopy method. All the relevant analytical data are recorded in Table 1.

Results and Discussion

The orange-red $Pd(INBA)_2$ and $Pd(INDBM)_2$ decompose at 150° and 190° respectively. The yellow-orange $Co(INBA)_3$ and $Co(INDBM)_3$ decompose at 210° and 195° respectively. 1:2 and 1:3 stoichiometry for palladium and cobalt complexes respectively were confirmed by elemental analysis and molecular weight determinations. All the complexes are soluble in solvents such as methanol, chloroform, benzene, acetone and ethylacetate. All solid complexes were found to be dimagnetic. This reveals that the palladium complexes must be planar in structure whereas cobalt complexes are octahedral involving d^2SP^3 hybridization. Bivalent cobalt gets oxidized to trivalent cobalt during complexation with isonitroso compounds.

The PMR spectrum of the HINBA and HINDBM in $CDCl_3$ show signals at 1.4 and 1.5 τ (with respect to TMS) respectively, which is assigned to the =NOH groups. HINBA exhibits methyl signals at 7.55 τ and phenyl signals at 2.18 – 2.62 τ. HINDBM exhibits bands at 1.88 – 2.64 τ. These bands are attributed to proton resonance signals from C_6H_5 groups. The integration of peak areas reveal that the ratio of the area under the peak at 1.5 τ to that under the peak at 1.88 – 2.64 τ approximates to ten. The metal complexes of both the ligands do not show any signal due to the =NOH group which indicates the replacement of the oxime proton by the metal during complexation.

The IR bands and their characteristic assignment are based on the study of the free ligands and their complexes. The strong and broad band around 3370–3300 cm^{-1} in ligands is attributed to hydrogen bonded -OH stretching frequency of the oxime group. The disappearance of this band in metal complexes suggests the replacement of the hydrogen of the oxime group by metal on complexation. This observation is in agreement with the results of PMR studies. One strong band at 1660-1650 cm^{-1} in metal complexes is assigned to C=O of aromatic ketone which indicates that the complexes are symmetric in nature. The weak band at 1620 cm^{-1} in the ligand is assigned to C=N

TABLE 1—PMR, UV AND ANALYTICAL DATA OF PALLADIUM AND COBALTIC COMPLEXES

Complex	Elemental analysis								PMR signals in τ with respect to TMS	Electronic absorption bands in kK (ϵ)	
	Calculated				Found					Methanol	Chloroform
	C	H	N	M	C	H	N	M			
HINBA	—	—	—	—	—	—	—	—	1.4, 2.18-2.62, 7.55	39.2	39.2
HINDBM	—	—	—	—	—	—	—	—	1.5, 1.88-2.64, —	39.0	39.4
Pd(INBA)$_2$	49.3	3.3	5.7	21.8	48.2	3.8	5.9	21.0	—, 2.34-2.70, 7.55	40.3(4999), 25.6(4700)	40.3(1693), 24.7(3725)
Co(INBA)$_3$	57.2	3.8	6.6	9.34	56.9	3.9	6.6	9.36	—, 2.00-2.60, 7.50	40.7(15630), 35.7(13110), 27.8(5771)	27.8(18870)
Pd(INDBM)$_2$	59.0	3.3	4.6	17.4	60.0	3.5	4.9	17.4	—, 2.20-2.80, —	39.4(6542), 25.0(3763)	39.4(24770), 24.3(25450)
Co(INDBM)$_3$	66.2	3.7	5.1	7.2	65.8	3.6	4.9	7.4	—, 1.80-2.80, —	—	27.8(41190)

stretching. The bands at 1595 and 1575 cm^{-1} in the complexes are attributed to perturbed C=O and or C=N stretching. The bands at 1575 cm^{-1} may also be assigned to C=C stretching frequency. The νNO observed in the region 1240–1225 cm^{-1} indicates that the coordination of the metal has taken through nitrogen of the oxime group. The bands at 612 and 600 cm^{-1} observed in Pd(INDBM)$_2$ an Co(INDBM)$_3$ complexes may be assigned to M-N vibration mode.

The electronic spectrum of HINBA and HINDBM in methanol and chloroform solution show one absorption band at 39.0–39.4 kK which may be assigned to $\pi-\pi^*$ transition in the ligand. The intensity of this band increases in Pd(INBA)$_2$ (40.3 kK, ϵ=4999 in CH_3OH; 40.3 kK, ϵ=1693 in $CHCl_3$), and Pd(INDBM)$_2$ (39.4 kK, ϵ=6542 in CH_3OH; 39.4 kK, ϵ=24770 in $CHCl_3$) complexes. Both Pd(INBA)$_2$ and Pd(INDBM)$_2$ in methanol show one more absorption band at 25.6 kK and 25.0 kK respectively which may be assigned to charge transfer transitions. In chloroform these band shift to 24.7 kK and 24.3 kK respectively. Co(INBA)$_3$ in methanol show three absorption bands. The bands at 40.7 kK (ϵ=15630) and 35.7 kK (ϵ=13110) may be attributed to $\pi-\pi^*$ transition whereas the charge transfer transition appears at 27.8 kK (ϵ=5771). Co(INBA)$_3$ and Co(INDBM)$_3$ in chloroform show charge transfer bands at 27.8 kK.

Acknowledgement

This Project was sponsored by the University Grants Commission, New Delhi, which awarded National Associateship to Dr. V. M. S. Authors also thank C. S. I. R, New Delhi, for awarding junior fellowship to one of them (B. J. D.) and to Dr. D. N. Sen of N.C.L., Poona for helpful discussions.

References

1. B. J. DESAI and V. M. SHINDE, *Analyst*, 1979, 140, 160.
2. B. J. DESAI and V. M. SHINDE, *Z. Anal. Chem.* 1979, 295, 412.
3. B. J. DESAI and V. M. SHINDE, *Z. Anal. Chem.*, 1979, 298, 158.
4. BEILSTEIN, Handbuch Der organische *Chemie*, Band VII, 864, 1409.

Potentiometric Studies of Complex Formation of Some Trivalent Rare Earths with 2-Hydroxy-1-Naphthalidene-2-Iminopyridine**

G. P. SENGUPTA* and C. R. BERA

Department of Chemistry, Visva-Bharati University, Santiniketan-731 235, W.B., India

Manuscript received 3 September 1979, accepted 30 December 1979

IN continuation to our earlier studies on Schiff-base ligands and their metal complexes[1,2], we report in the present communication our potentiometric studies of the proton-ligand stability constants of 2-hydroxy-1-naphthalidene-2-iminopyridine and its formation of 1:1 complexes with Pr(III), Nd(III), Sm(III) and Gd(III).

All chemicals and reagents used in the study were either of A.R. grade or purified before use.

The Schiff-base ligand was prepared by an analogous method as described in our earlier paper[2]. The purity of the ligand was checked by elemental analysis and melting point determination.

Carbonate free sodium hydroxide solution[3] and double distilled water were used. Rare earth metals were converted to perchlorates and were estimated by EDTA method[4]. The metal perchlorates were dissolved in 0.1M $HClO_4$ to avoid metal hydrolysis.

A digital pH-meter of Electronics Corporation of India, model No. pH-5651 (accuracy $\pm$0.01 unit) with combined glass electrode assembly was used for the present study. All computation works were done in programmable calculator (EC 62 p) of Electronics Corporation of India.

**Presented in the "Annual Convention of Chemists" 1979 at Kurukshetra.

Bjerrum – Calvin[5,6] pH-titration technique as adopted by Irving-Rossotti[7] was followed to determine the formation constant values. Following sets of titrations were performed at a constant ionic strength $0.1M$ $NaClO_4$ in 50% (v/v) acetone-water medium at $30\pm1°$.

i) 10 ml $0.1M$ $HClO_4$ + 5 ml $1M$ $NaClO_4$ + 10 ml water + 25 ml acetone.

ii) Solution mixture (i) $+4\times10^{-3}M$ ligand.

iii) 5 ml $0.1M$ $HClO_4$ + 5 ml $1M$ $NaClO_4$ + 5 ml $0.01M$ metal solution + $4\times10^{-3}M$ ligand + 25 ml acetone + 10 ml water.

The total volume in each case was kept constant (50 ml) initially and the ratio of metal salt to reagent was maintained at nearly 1:4 in all titrations in order to satisfy the maximum coordination possibility of the metal ions.

From the titration curves using solutions (i) and (ii), $\bar{n}_H$ values at various "B" values (pH-meter readings) were calculated and the formation curve between "B" and corresponding $\bar{n}_H$ was plotted [Fig. 1A]. The

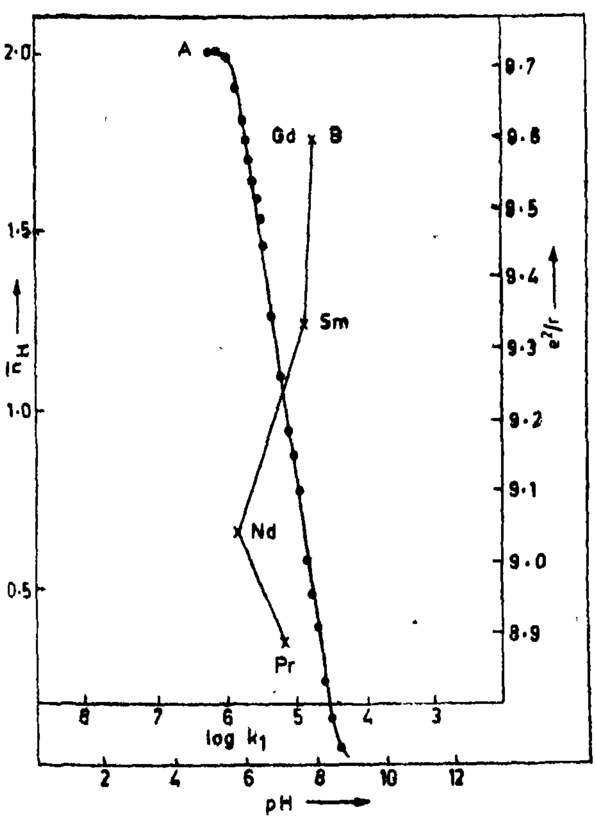


Fig. 1. A-Plot of $\bar{n}_H$ against pH-meter reading.
B-Plot of e^2/r against log K_1 values.

values for the "practical" proton-ligand stability constants log $^PK_1^H$ and log $^PK_2^H$ were evaluated by using (i) Bjerrum's half-integral method and (ii) pointwise calculation method[8]. The values agree closely. In the light of our discussion in the earlier paper[8], log $^PK_1^H$ value (7.8) has been assigned to the proton dissociation of the phenolic OH and the log $^PK_2^H$ value (6.4) to the proton-affinity value of the pyridine nitrogen of the Schiff base ligand under study.

From the titration curves using solutions (ii) and (iii), $\bar{n}$ (metal-ligand formation, number) and PL(free ligand concentration) were calculated by using the following relations :

$$\bar{n}=\frac{(V'''-V'')\,(N°+B°)}{(V°+V')\,T_c^oM}\times\frac{1}{\bar{n}_H} \qquad \ldots (1)$$

(where T_c^oM denote the total concentration of metal present in the solution and other terms have their usual meanings) and

$$PL=\log\frac{\left[\sum_{n=0}^{n=J}\beta_n^H(1/\text{anti log B})^n\,(V°+V''')\right]}{[(TcL°-\bar{n}TcM°)\,V°]} \quad \ldots (2)$$

(where β_n^H is the overall "practical" proton–ligand stability constant). The $\bar{n}$ values were plotted against the corresponding pL values to get the metal ligand formation curves (Fig. 2). The values of metal-ligand stability constant log K_1 were calculated by (i) pointwise calculation and (ii) Bjerrum half-integral method. The values are shown in Table 1.

TABLE 1—STABILITY CONSTANT OF 2-HYDROXY-1-NAPHTHALIDENE-2-IMINOPYRIDINE WITH RARE EARTH METALS AT $\mu=0.1M$ $NaClO_4$ IN 50% (v/v) ACETONE-WATER MEDIUM AT $(30°\pm1°)$

	H+ log $^PK_1^H$	log $^PK_2^H$	Pr(III)	Nd(III)	Sm(III)	Gd(III)
Bjerrum half $\bar{n}$ method	7.800	6.430	5.100	5.900	4.850	4.80
Pointwise calculation	7.875	6.412	5.100	5.875	4.950	4.875
log β_n		14.259	5.100	5.888	4.900	4.838

The maximum value of $\bar{n}$ was near about 0.8 and this indicates 1:1 complexation below the region of metal hydrolysis. The order of stabilities of metal complexes is Gd(III)<Sm(III)<Pr(III)<Nd(III).

Rare earths, with their 4f orbitals being well-shielded, usually form ionic compounds and are expected to obey the Born relationship[9]. The possibility of some covalent interaction, however, cannot be completely excluded as reported in the case of acetylacetone complexes of rare-earths[10]. In the present study, the log K_1 values of 1:1 metal-ligand complexes have been plotted against e^2/r (Fig. 1 B). Though some amount

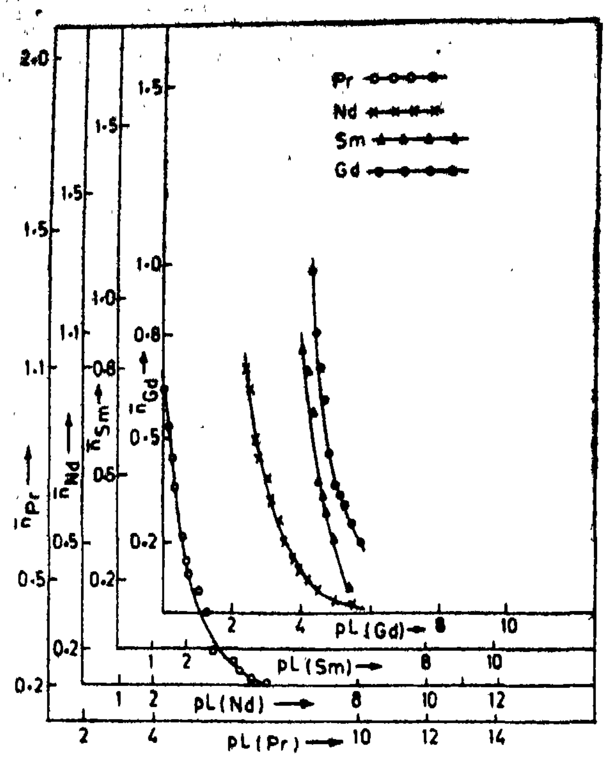


Fig. 2. Metal-ligand formation curves.

of ionic character may be suggested to the metal-ligand bonding, the plots, however, do not exhibit any complete linear relationship. Such a difference in the trend of stability constant is not uncommon in the case of lanthanide complexes[11-13] and this may be due to varying degree of stabilization arising out of interaction of 4f metal orbitals with the ligand field[14].

The absence of 1:2 chelates in the present case may be due to steric hindrance produced by the attached ligand in the 1:1 chelate to the approach of the second one.

Acknowledgement

Thanks are due to the U.G.C and the Visva-Bharati University for the award of a Junior Research Fellowship to one of the authors (C.R.B.).

References

1. R. L. Dutta and G. P. Sengupta, *J. Indian Chem. Soc.*, 1971, 48, 83.
2. C. R. Bera, S. Chattopadhyay and G. P. Sengupta, *J. Indian Chem. Soc.*, 1979, 56, 416.
3. A. I. Vogel, "Quantitative Inorganic Analysis" Longman Publication, London, 1961, p. 239.
4. G. Schwarzenbach, "Complexometric Titrations" Methuen & Co. Ltd. London, 1956, p. 60.
5. J. Bjerrum, "Metal Ammine Formation in Aqueous Solution" P. Hasse, Copenhagen, 1941.
6. M. Calvin and K. W. Wilson, *J. Amer. Chem. Soc.*, 1945, 67, 2003.
7. H. M. Irving and H. S. Rossotti, *J. Chem. Soc.*, 1954, 2904.
8. K. B. Jabalpurwala, K. A. Venkatachalam and M.B. Kabadi, *J. Inorg. Nuclear Chem.*, 1964, 26, 1011.
9. R. A. Robinson and R. H. Stokes, "Electrolytic Solutions", (Butterworths, London), 1959, 355.
10. T. Moeller, D.F. Martin, L. C. Thompson, R. Ferrus, G. R. Feistel and W. J. Randall, *Chem. Rev.*, 1965, 65, 1.
11. F. H. Spedding, J. E. Powel and E. J. Wheelwright, *J. Amer. Chem. Soc.*, 1956, 78, 34.
12. J. Schwarzenbach and R. Gut, *Helv. Chim. Acta*, 1956, 39, 1589.
13. R. C. Vickery, *J. Molec. Spectrosc.*, 1956, 2, 308.
14. L. K. A. Stavely and T. Randall, *Discussions Faraday Soc.*, 1958, 26, 157

Potentiometric Studies of Metal Chelates of Tiron with Be(II), Cu(II) and Al(III)

B. C. BHUYAN and S. N. DUBEY*

Department of Chemistry, Kurukshetra University, Kurukshetra-132 119

Manuscript received 19 September 1978, revised 13 September 1979, accepted 4 March 1980

Although chelating properties of tiron have been reported with a number of metals[1-5], no attempt appears to have been made to determine the thermodynamic stability constants of its chelates with Be(II), Cu(II) and Al(III). In the present communication, the proton-ligand stability constants of tiron, the thermodynamic stability constants of its chelates with Be(II), Cu(II) and Al(III) and thermodynamic changes ($\triangle G$, $\triangle H$ and $\triangle S$) accompanying complex formation have been reported.

Experimental

The solution of beryllium sulphate (Russian), copper sulphate (BDH, AR) and aluminium nitrate (E. Merck) were prepared in double distilled water and standardised by standard analytical methods. The solutions of tiron (Hopkins and Williams, England) and sodium perchlorate (Riedel) were also prepared in double distilled water. The *p*H-titrations were carried out at varying ionic strengths (0.1, 0.2 and 0.3*M*) and temperatures (30° and 40°) with a Philips precision *p*H meter (PR 9405M) using standard glass and calomel electrodes.

Results and Discussion

The Calvin Bjerrum titration technique[4,5] as modified by Irving and Rossotti[6] has been used to

* To whom correspondence should be made.

TABLE 1—THE FORMATION CONSTANTS AND THERMODYNAMIC FUNCTIONS OF TIRON COMPLEXES WITH Be(II), Cu(II) and Al(III)

Metal ion	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_1$	$\log K_2$	$\log K_3$
	30°, μ=0.1 *M*			30°, μ=0.2 *M*			30°, μ=0.3 *M*			40°, μ=0.1 *M*		
H^{+}	11.05	7.75	—	10.85	7.63	—	10.67	7.56	—	10.67	7.60	—
Be^{2+}	12.51	10.66	—	12.18	10.17	—	11.04	9.17	—	11.18	8.23	—
Cu^{2+}	15.08	13.69	—	14.80	13.34	—	14.14	12.76	—	13.70	12.30	—
Al^{3+}	15.48	14.61	12.72	14.78	13.92	12.43	14.39	13.48	12.15	15.33	14.36	12.45

	Δ G (k. cal./mole)		Δ H (k. cal./mole)	Δ S (e. u.)
	30°C	40°C	30°C	35°C
Be^{2+}	−32.67	−27.37	−163.34	−424.04
Cu^{2+}	−40.57	−36.66	−120.33	−258.86
Al^{3+}	−60.37	−59.42	−29.22	98.36

The thermodynamic formation constants log $K^{\mu=0}$ for Be (II), Cu(II) and Al (III)-tiron complexes were found to be 13.24, 11.50, 15.63, 14.04, 16.00. 15.18 and 13.00 respectively.

determine the formation constants of tiron and the formation constants of its complexes with Be(II), Cu(II) and Al(III). The log K values were further computed by different computational techniques[7,8] and the mean values are given in Table 1. The thermodynamic formation constants were evaluated by extrapolating the determined formation constants to zero ionic strength and are given at the bottom of Table 1.

The values of overall changes in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) accompanying complex formation were calculated using standard equations[9] (Table 1).

A comparison of stepwise formation constants reveals that stability decreases with increase in ionic strength and temperature i.e., lower temperature is favourable for complex formation. The order of stability follows Al(III) > Cu(II) > Be(II). The same has also been observed by other workers[10] with polyhydroxy ligands.

The positive entropy change in case of Al(III) is ascribed due to extensive hydration of Al(III) ion in aqueous solution which releases large number of water molecules on complexation and it may be one of the reasons which accounts for the greater stability of Al(III)-tiron complexes to Be (II)-and Cu (II)-tiron complexes.

Acknowledgement

The authors are thankful to Prof. H. L. Bhatnagar, Head of the Department of Chemistry, Kurukshetra University, for providing facilities, and one of us (B.C.B.) is also thankful to the U.G.C. for granting a Teacher Fellowship.

References

1. MARIA FABRIZIA LANDI, *Ric. Sci. Red. Sez.*, 1964, A7(1), 165 ; 1964, A7(3), 671.
2. R. C. NAND, R. C. DASS and R. K. NANDA, *Indian J. Chem.*, 1965, 3(6), 278.
3. M. BARTUSCK and L. SOMMER, *J. Inorg. Nuclear Chem.*, 1965, 3(6), 2397.
4. M. CALVIN and K. W. WILSON, *J Amer. Chem. Soc.*, 1945, 67, 2003.
5. J. BJERRUM, "Metal amine formation in aqueous solution", P. Haase and Son., 1941.
6. H. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.*, 1954, 2904.
7. H. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.*, 1953, 3397.
8. S. N. DUBEY and R. C. MEHROTRA, *Indian J. Chem.*, 1967, 5, 327.
9. K. B. YATSIMIRSKII and V. P. BASIL'EV, 'Instability Constants of Complex Compounds', Pergamon Press, London, 1960, p. 59.
10. S. N. DUBEY, Ph.D. Thesis, University of Rajasthan, Jaipur, 1965.

Extractive Spectrophotometric Determination of Iron(III) with N-Hydroxy-N-Phenyl-N′-o-Chlorophenyl-p-Toluamidine Hydrochloride in Presence of Thiocyanate**

(Miss) HEMLATA MOHABEY

and

RAJENDRA K. MISHRA*

Department of Chemistry, Ravishankar University, Raipur-492 002 (M.P.)

Manuscript received 31 March 1979, revised 21 January 1980, accepted 4 March 1980

THIOCYANATE method[1] is frequently used for colorimetric determination of Iron(III) but suffers from various limitations such as stability, reproducibility, nonlinearity of Beer's law, amount of thiocyanate etc. These make its routine use difficult. Even the modified method lacks selectivity[2]. The method[3] based on the ternary complex formation of Iron(III) with N-hydroxyethylenediamine N, N′, N″-triacetate is fairly selective but lacks sensitivity. N-hydroxy-N, N′ diarylbenzamidines are new types of organoanalytical reagents[4]. The present paper reports the use of a newly synthesised hydroxyamidine, N-hydroxy-N-phenyl-N′-o-chlorophenyl-p-toluamidine hydrochloride (HPCPTH) which reacts with Iron(III), forming a benzene extractable orange red complex in thiocyanate medium. On this basis a simple, rapid and sensitive spectrophotometric method has been developed for the determination of microgram quantities of Iron(III). The method is highly selective as Fe(II) and almost all common ions including those which usually interfere with the parent thiocyanate method and other literature methods do not interfere.

Experimental

Apparatus: Absorbance values were measured with an ECIL UV-VIS spectrophotometer model GS-865 using 1 cm matched quartz and silica cells.

Reagents and Chemicals: All the chemicals used were of A. R. grade.

The reagent (HPCPTH) was prepared by the condensation of equimolar quantities of N-o-chlorophenyl-p-toluimidoyl chloride and N-phenylhydroxylamine in ether medium. The resulting hydrochloride was crystallised from absolute alcohol containing a few drops of concentrated hydrochloric acid. (Yield 75%). Found: C, 64.55%; H, 5.04%; N, 7.60%; Calculated for $C_{20}H_{18}N_2OCl_2$; C, 64.3%; H, 4.8%; N, 7.506%.

A stock solution of Iron(III) was obtained by dissolving 0.5 g of pure iron wire (E. Merck, A. R.) in 1:3 nitric acid. It was boiled to expel oxides of nitrogen and standardised gravimetrically. A 5% (w/v) solution of potassium thiocyanate was used.

Procedure: An aliquot of Iron(III) solution containing 50 μg of metal was taken in a 125 ml separatory funnel. A 2 ml of 5% (w/v) thiocyanate was added. Adjusted the acidity to 0.25 – 0.70 *M* hydrochloric acid in final dilution of 25 ml. The solution was equilibrated for 2 minutes with 25 ml of 0.1% benzene solution of HPCPTH. The orangered benzene layer was dried over anhydrous sodium sulphate and the absorbance values were measured at 460 nm against reagent blank.

Results and Discussion

The absorbance of the ternary Iron(III)-HPCPTH-SCN complex was maximum at 460-470 nm with molar absorptivity 12300 l. $mole^{-1}$ cm^{-1} in benzene. The reagent, under similar conditions showed negligible absorbance in the region 450-700 nm.

Beer's law was obeyed upto 4.8 ppm of Iron(III) at 460 nm and the optimum concentration range on the basis of Ringbom plot was 0.8 to 4.0 ppm of metal. The Sandell's sensitivity of the colour reaction was 0.0045 μg Iron(III) per cm^2. The standard deviation and the relative standard deviation of the method were found to be $\pm$ 3.75×10^{-3} and $\pm$ 0.85% respectively with mean absorbance 0.44 unit for 15 measurements, each containing 50 μg Iron(III)/25 ml.

Effect of Variables: The maximum colour intensity was obtained in the range of 0.25-0.70 *M* hydrochloric acid medium. Below 0.25 and beyond 0.70 *M* hydrochloric acid concentration low absorbance values were obtained and the rate of extraction decreased with increase in acidity of the aqueous phase.

Various solvents like benzene, toluene, chloroform, carbon tetrachloride etc. extracted the mixed chelate. Benzene was found to be the best as the ternary complex showed high distribution ratio in it.

A 25 fold and 130 fold molar excess of HPCPTH and thiocyanate were adequate for complete extraction of Iron(III). Order of addition of reagents was not critical. Excess reagents caused no adverse effect in the determination of Iron(III). A time of two minutes was sufficient for complete extraction of the thiocyanate mixed chelate. Variation of temperature from 20° to 30° did not affect the absorbance of the coloured system. The complex was stable for at least 30 hrs at 27 $\pm$ 2°.

Composition: The composition of Iron(III)-HPCPTH-thiocyanate was determined by curve fitting method[5]. The results obtained showed the formation 1:1:2 (metal : reagent : thiocyanate) mixed complex in benzene.

**Presented at Convention of Chemists 1978.

*Senior Author.

Interferences : In the determination of Iron(III) at 0.4 *M* hydrochloric acid the effect of diverse ions were studied as described in earlier procedure. Chloride, bromide, ammonia, urea, thiourea, phthalate, nitrate, sulphate, alkali metals, alkaline earth metals and lanthenoid elements had no interfering effect upto 2000 ppm. The tolerance limits of other ions causing an error less than 2% are shown in parenthesis (in ppm): phosphate (1200), fluoride (1400), arsenate (1600), UO_2^{2+}, Mn^{2+}(600), Fe^{2+}, Co^{2+}, Cr^{3+}(800), Ni^{2+}(2000), Zn^{2+}, Cd^{2+}(1600), Zr^{4+}(400), W^{6+}(200), Mo^{6+}(15), V^{5+}(50), Al^{3+}(1200), Cu^{2+}(10), Ti^{4+}(50), Ta^{5+}(200).

Acknowledgement

The authors are thankful to Dr. S. G. Tandon, Head, Department of Chemistry, Ravishankar University, Raipur for providing research facilities.

References

1. E. B. SANDELL, "Colorimetric Determination of Traces of Metals", Interscience Publishers Inc., New York, 1956, p. 524, 537, 544.
2. I. M. KOLTHOFF and E. B. SANDELL, "A Text Book of Quantitative Inorganic Analysis", The MacMillan Co., New York, 1952, p. 636.
3. K. YAMAMOTO and K. OHASHI, *Anal. Chim. Acta*, 1977, 88, 141.
4. K. SATYANARAYANA and R. K. MISHRA, *J. Indian Chem. Soc.*, 1976, 53, 63.
5. L. G. SILLEN, *Acta Chem. Scand.*, 1956, 10, 185.

Morpholine-4-Carbodithioate as a Gravimetric Reagent for Indium(III)

NEPAL SINGH, R. C. AGARWAL and B. D. KANSAL

Department of Chemistry, Hindu College, Moradabad

Manuscript received 25 September 1978, revised 10 October 1979, accepted 4 March 1980

INDIUM(III) has been precipitated quantitatively in *p*H range 4.4–6.7 as morpholine-4-carbodithioate complex of composition $[(C_5H_8ONS_2)_3In]$ which can be weighed after drying at 110–120°. The effect of several diverse ions on precipitation was avoided using suitable masking agents.

Numerous organic reagents employed for the estimation of Indium(III) are described[1-5]. In continuation of our investigations[6-9] here we report the application of bidentate morpholine-4-carbodithioate as new gravimetric reagent for Indium(III) and its separation from a number of ions using ammoniacal EDTA as masking agent.

Experimental

The potassium salt of the reagent morpholine-4-carbodithioate has been prepared by treating morpholine in dry ether at 0° with carbon-disulphide and adding potassium hydroxide during four hours under vigorous stirring (Molar ratio ; Morpholine : Carbon disulphide and Potassium hydroxide is 1:1:1). The crude product was recrystallised from iso-propyl alcohol. The solution of indium trichloride was prepared by usual method.

Procedure for the determination of In(III) :

An aliquot of the Indium(III) solution (0.02*M*) was diluted to about 150 ml with distilled water. The *p*H of the solution was adjusted to 5.0 by adding appropriate quantity of acetate buffer. The 1% reagent (MCDT) solution (w/v) in distilled water was then added with constant stirring. A white precipitate gradually separates out which was digested on water-bath (60-65°) for about 20 minutes. The precipitate was filtered through sintered crucible (G-4), washed with distilled water and dried at 110-120°.

Effect of foreign ions on the determination of In(III) :

To study the influence of foreign ions on gravimetric determination of In(III), a definite amount of various anions and cations (2-4 fold) were added to a definite quantity of In(III) solution prior to the addition of reagent (MCDT). The *p*H of the solution was adjusted to 5 – 5.5 using acetate buffer and estimations were carried out as described earlier. It was found that the ions Ba(II), Ca(II), Sr(II), Mg(II), Be(II), Al(III), Th(IV), Zr(IV), NO_3^-, CH_3COO^-, Cl^-, Br^-, I^-, citrate, tartrate do not interfere in quantitative determination of Indium(III). The ions $C_2O_4^{2-}$, PO_4^{3-} and BO_3^{3-} interfere. A mixture of ammoniacal EDTA and tartrate masked Tl(I), Co(II), Fe(II), Zn(II), Cd(II), Sn(II), Fe(III), In(III) and Ga(III), therefore could not be determined in presence of each other. The ions Ag(I), Hg(II), Pb(II), Cu(II), Pd(II) and Bi(III) precipitate at the same *p*H range, therefore create interference in their determination. To overcome this difficulty an ammoniacal mixture of EDTA and tartrate is used as masking agent for In(III) before the precipitation of aforesaid ions. The Indium(III) can be demasked by repeated treatment with HNO_3 (dilution and evaporation) and determine Indium(III) using morpholine-4-carbodithioate after neutralizing the adhering nitric acid.

The Indium(III) complex is thermally stable upto 180°. The precipitate settles within few minutes and requires less time for digestion. The digestion above 80° yield low results. It is due to the fact that In(III) dithiocarbamate in contact with water get slightly dissolved. The negative results in estimation of indium might be due to slight solubility of the In(III) chelate. The percentage of negative error varies from -0.26 to -0.29 when the complex was heated at 50—70° (digestion

time 20 – 30 minutes). The negative error exceeds to -0.38% when the duration of digestion is an hour at 80°.

The positive error for indium was observed in binary mixture of Hg(II) and In(III) only. Mercury(II) was estimated by masking In(III) with ammoniacal EDTA. The positive error might be due to slight solubility of Hg(II) dithiocarbamate in ammoniacal EDTA which is coprecipitated later on. The results of Hg(II) are better than -0.5%. The error of indium(III) dithiocarbamate varies in between + 0 18 to + 0.24%. The determination of indium in binary mixture (Ag, Hg, Pb, Cu and Bi) required acid treatment which makes the estimation slightly lengthier, inspite of this, the determination of indium is fast and accurate.

References

1. E. N. VINOGRADOVA and N. N. CHUDINOVA, *Zarodskaya*, 1956, **22**, 1280.
2. P. SAKELLARIDIS and E. PAPARICOLAOU, *Chim. Chromika (Athens Greeca)*, 1961, **26**, 163.
3. A. M. GOLUB and V. M. SAMOILENKO, *Urk, Khim, Zh.*, 1963, **29**(5), 472.
4. E. P. FRANCA and R. W. DODSON, *J. Amer. Chem. Soc.*, 1955, **77**, 2651.
5. P. SENISE *et al.*, *J. Amer. Chem. Soc.*, 1961, **83**, 4146.
6. N. SINGH, R. KUMAR and B. D. KANSAL, *J. Indian Chem. Soc.*, 1978, **55**, 240.
7. N. SINGH, R. KUMAR and R. C. AGARWAL, *J. Indian Chem. Soc.*, 1978, **55**, 961.
8. N. SINGH, R. C. AGARWAL and V. K. MAHESHWARI, *J. Indian Chem. Soc.*, 1978, **55**, 961.
9. G. ST. NICOLOV, N. JORDONOV and HAVENGOV, *J. Inorg. Nuclear Chem.*, 1971, **33**, 1056.

Solvent Extraction Studies of Vanadium(V) in presence of N-*p*-methoxybenzoyl-N-*p*-methyl-phenylhydroxylamine and Thiocyanate

SASWATI P. BAG and SUKAMAL SAHA

Department of Chemistry, Jadavpur University, Calcutta-700 032, India

Manuscript received 7 November 1978, revised 6 September 1979, accepted 18 March 1980

THE recent interest in mixed-ligand complexes has stimulated the development of new methods of separation and analysis of metals[1-4].

Binary complexes of vanadium(V)-arylhydroxylamine systems[5,6] produce blue/reddish-violet 1:2 complexes having the absorption maxima between 510-530 nm. A few mixed-ligand vanadium(V)-oxinate complexes[7,8] have also been reported.

An account of the spectrophotometric studies on the formation of a ternary complex of vanadium(V) with N-*p*-methoxybenzoyl-N-*p*-methyl-phenylhydroxylamine (I)[9] and thiocyanate is presented in this paper. The reagent (I) is found to form extractable blue-violet binary complex (λ_{max} at 540 nm at high acidity) with the metal. The extraction of the dark blue-violet vanadium(V) mixed-ligand complex in presence of thiocyanate takes place in the *p*H range (0.8-2.2) as well as in the acid range of 2-4*N* HCl and is stable over 4 hours at room temperature. The complex absorbs maximum at 570 nm. A hyperchromic effect followed by bathochromic shift in the absorption maxima occurred for the formation of mixed-ligand complex. Different extraction constants (log K_{ex}, log K_d and log $K_{d(mixed)}$) have been evaluated.

Experimental

Reagents, Solutions and Apparatus :

The reagent (I) (m.p. 128-30°) was prepared following the method described in monograph[6]. Solutions of the reagent (I) was prepared in A.R. chloroform.

An aqueous solution of vanadium(V) was prepared from A.R. ammonium meta-vanadate and the solution was standardised volumetrically[10].

All the reagents, chemicals, solvents etc. used in the spectrophotometric measurements were of A.R. grade or spectro-grade quality.

A Hilger Uvispek spectrophotometer with 1.0 cm glass cells was used for the absorbance measurements. All *p*H-measurements were made with Elico (model LI-10) *p*H meter.

Extraction Procedure of Vanadium(V) :

An aliquot of the metal solution (1 ml of 0.1 mg/ml solution) was transferred into 100 ml of separatory funnel, followed by dilute acid (6*N* HCl) and water to achieve *p*H 1.8 and the aqueous phase of 15 ml. 5 ml of 0.5% (w/v) reagent(I) solution and 10 ml chloroform were added and shaken for 10 minutes. To this solution, 5 ml of 2% standard ammonium thiocyanate solution was added and the mixture was thoroughly shaken for another 5 minutes. The resultant dark blue-violet complex in the chloroform layer was drained out and the aqueous layer was washed twice with 5 ml portion of the solvent, the extracts, combined dried and transferred to a 25 ml standard flask. The volume was made up with the solvent and the absorbance was measured at 570 nm against chloroform as blank.

Results and Discussion

Absorbance Spectra : The absorbance spectra of the mixed complex [V(V) – I – SCN] [V(V) = 7.86 × 10^{-5} *M*] extracted in chloroform at *p*H 1.8 shows maximum absorption at 430 nm and 570 nm. Subsequent measurements were made at 570 nm against solvent as blank where the reagent had no absorption.

Effect of Acid Concentration : The stable mixed-ligand complex is formed at both pH (0.8-2.2) and high acidity (2-4N HCl) ranges, having same absorption maxima, molar absorptivity (ϵ=7260 l mol^{-1} cm^{-1} at 570nm) and the Sandell's[12] sensitivity (0.007μgV/cm^2).

Effect of Reagent (thiocyanate) : For the formation of mixed complex of V(V), 5 ml of 1% ammonium thiocyanate solution was found sufficient for full development of color for 4 ppm of the metal. Very large excess of thiocyanate concentration or simultaneous addition with ligand decreases the color intensity.

Calibration curve, Optimum range and Photometric error :

It is found that the system obeys Beer's law over the concentration range of 0.5-12 ppm and the optimum concentration range as obtained from the Ringbom's[13] plot is from 1-10 ppm. The relative analysis error per 1% absolute photometric error according to Ayres[13] equation is found to be 2.70 in all the cases.

Effect of diverse ions : Interferences due to different ions were less at high acidity in comparison to that at low pH range. So during analysis, the interferences were minimised by adjusting the acidity. Ti(IV), Fe(III), Cu(II), W(VI), Mo(VI), Nb(V), Zr(IV) interfere with different tolerance limits. Heavier transition metals like Os(VIII), Re(VII), Pd(II) and Pt(IV) were found to interfere. Tolerance limit of Ti(IV) could be increased by using NaF and the interference due to Fe(III) might be avoided either by increasing acid concentration of the solution or by extracting it in solvent ether at 6-8N HCl. Mo(VI) was removed by ethyl-xanthate extraction[14]. Tolerance limit of W(VI) and Zr(IV) was increased by the addition of phosphate and that of Cu(II) and Cr(III) was increased by the addition of EDTA at low acidity.

Procedure for High Speed Steel Analysis :

(BAS, 64b) – contains 1.99% of V.

0.6g of the sample was dissolved in dilute H_2SO_4 (1:4) and evaporated to a syrupy mass, repeating the process twice with 5 ml portion of concentrated H_2SO_4 and once with 5 ml concentrated HNO_3. The solution was heated to dense white fumes, cooled, diluted to 50 ml and then boiled to dissolve any solid matter. It was filtered and the residue washed several times with hot water. The solution was made upto 250 ml volume in a standard flask.

Transfer an aliquot of the solution and oxidise with 0.1% $KMnO_4$ solution. The general procedure was followed for extraction and the extract was washed with 2N HCl to back extract Fe(III) into the aqueous phase. The absorbance of the extract thus obtained was measured at 570 nm and the percentage of vanadium in the sample was found to be 1.950%.

Composition and Extraction Constants of the Mixed-Ligand Complex System :

In view of finding the ratio of metal to reagent (*I*) in presence of a constant excess of thiocyanate solution both Job's[15] and molar ratio[16] method as well as absorptiometric method[7,8,17,18] are applicable.

For Job's and molar ratio methods, equimolar solutions (9.825×10^{-4}M) of vanadium(V) and reagent (I) in chloroform were used and a fixed concentration of thiocyanate (5 ml of 2% solution for each extraction) was maintained. The experimental plot indicates the metal to ligand ratio as 1:2. The result is verified absorptiometrically i.e., from the plot of $\log\frac{E}{E_{max}\ E} - pH$ vs $\log\ [HR]_{org}$ and the $\log K_{ex}$ is thus obtained from the intercept on the ordinate and the value is 6.20, using the equation :

$$K_{ex} = \frac{[VO(R)_2OH]_{org}\ [H^+]}{[VO_2^+]_{aq}\ [HR]^2_{org}} = \frac{D_0[H^+]}{[HR]^2_{org}} \text{ where } D_0$$

$$= \frac{[VO(R)_2OH]_{org}}{[VO_2^+]_{aq}} = \frac{E}{E_{max} - E}$$

and E_{max} = maximum absorption

E = absorption for the amount of HR at the point in question.

The above relation can be represnted as,

$$\log\frac{E}{E_{max} - E} - pH = \log K_{ex} + 2\log\ [HR]_{org}$$

The ratio of vanadium(V) to thiocyanate could not be determined by applying Job's and molar ratio methods but was determined absorptiometrically. The measurement of absorbance of the extracts obtained by varying the concentration of thiocyanate (under respective λ_{max} and pH) at a constant excess of I (5 ml of 0.5% solution in chloroform for each extraction) and V(V) of 7.86×10^{-5}M, the plot of $\log\frac{E_A - E_{min}}{E_{max} - E_A}$ vs log [SCN$^-$] – pH gave a st. line with a slope of unity which indicates the metal : thiocyanate ratio as 1:1 and the $\log K_A$ is obtained from the intercept by extrapolation and the value is 4.88.

Hence the equilibrium extraction constant of the mixed-ligand system, $\log K_{mixed}$ at room temperature is obtained from $\log (K_{ex}\ K_A)$ and the value is 11.08. The $\log K_{mixed}$ was also determined directly from the absorptiometric plot of $\log\frac{E}{E_{max} - E}$ vs $2\log[HR]_{org}$ + log [SCN$^-$] – pH, gave a st. line and the value is obtained from the intercept by extrapolation and is found to be 11.0.

K_A and K_{mixed} are determined using the equations :

$$K_A = \frac{[VO(R)_2\ SCN]_{org}}{[VO(R)_2\ OH]_{org}\ [SCN^-]\ [H^+]},$$

(which is equivalent to)

$$\log_{\epsilon} \frac{E_A - E_{min}}{E_{max} - E_A} = \log K_A + \log\ [SCN^-] - pH$$

and

$$\log D_{mixed} = \log \frac{E}{E_{max} - E} = \log K_{mixed}$$

$$+ 2 \log\ [HR]_{org} + \log\ [SCN^-] - pH.$$

The value of log K_{mixed} is quite in agreement with the previous result.

References

1. A. T. PILIPENKO and M. M. TANANAIKO, *Talanta*, 1974, 21(6), 501.
2. GEORGE K. SCHWEITZER and W. VAN WILLIES, *Anal. Chim. Acta*, 1964, 30, 114.
3. C. WOODWARD and H. FREISER, *Anal. Chem.*, 1968, 40, 345.
4. S. OKI and I. TERADA, *Anal. Chim. Acta*, 1972, 61, 49.
5. I. P. ALIMARIN, F. P. SUDAKOV and B. G. GOLOVKIN, *Russ. Chem. Rev.*, 1962, 31, 466.
6. A. K. MAJUMDAR, "N-Benzoylphenylhydroxylamine and Its Analogues", Pergamon, Oxford, 1972.
7. I. KOJIMA and M. TANAKA, (i) *J. Inorg. Nuclear Chem.*, 1967, 29, 1769 ; (ii) *Anal. Chim. Acta*, 1975, 75(2), 367.
8. Y. ANJANEYULU, B. SIVA RAMA SARMA and V. PANDU RANGA RAO, *J. Indian Chem. Soc.*, 1977, 54, 596 and references therein.
9. U. TANDON and S. G. TANDON, *Analyst.*, 1961, 86, 544.
10. A. I. VOGEL, "Quantitative Inorganic Analysis", 3rd ed., Longman's Green and Co., London, 1964.
11. E. B. SANDELL, "Colorimetric determination of trace metals", Interscience Publishers, Inc., New York, 3rd Ed., 1959.
12. A. RINGBOM, *Z. Anal. Chem.*, 1938, 115, 332.
13. G. H. AYRES, *Anal Chem.*, 1949, 21, 652.
14. B. T. KENNA, *Anal. Chem.*, 1960, 33, 1130.
15. P. JOB, *Ann. Chim.* (Paris), 1928, 9, 113.
16. J. H. YOE and A. L. JONES, *Ind. Eng. Chem. Anal. Ed.*, 1944, 16, 111.
17. C. F. HISKEY and V. W. MELOCHE, *J. Amer. Chem. Soc.*, 1940, 62, 1565.
18. I. KOJIMA and M. TANAKA, *Anal. Chim. Acta* 1966, 36, 522.

Leucoanthocyanins from *Cassia javanica* Root Bark

J. SINGH and R. D. TIWARI

Chemical Laboratories, Allahabad University, Allahabad, India

Manuscript received 12 September 1979, accepted 18 March 1980

FROM the ethanolic extract of the root bark of *Cassia javanica* two anthraquinones and their glycosides had been isolated and the chemistry of these compounds reported earlier[1].

In the present communication isolation and structural studies of two new leucoanthocyanins (I) and (II) are being reported.

Plant of the genus *Cassia* are well known for their medicinal value[2] and are also rich sources of flavonoids and anthraquinones[3,4,5].

The root bark of *Cassia javanica* was collected from a matured tree in the University campus. The dried powdered root bark was extracted with acetone, the extract concentrated under reduced pressure and poured into excess of cold water when a brown mass deposited which was filtered. The precipitate and filtrate were worked up separately.

The water insoluble portion was extracted with ether and ethyl acetate respectively. Ether fraction contained a flavonol, quercetin, which was confirmed by mp, mmp, derivatization and spectral studies[6]. Ethyl acetate fraction was concentrated and light petrol (40-60) was gradually added and the coloured sticky solid first separating was discarded. Further addition of petrol yielded the leucocyanin(I). The process was repeated several times in order to obtain an almost colourless sample, m. p. 290°(d.).

The water soluble portion was concentrated under reduced pressure and extracted with ethyl acetate in a continuous liquid-liquid extractor. Ethyl acetate extract was concentrated and petrol was gradually added and the coloured sticky solid first separated was discarded. Further addition of petrol yielded leucopeonin(II). The process was repeated several times till pure leucopeonin was obtained, melting at 200°(d.).

Leucocyanin (Compound I) :

Compound (I) $C_{21}H_{24}O_{11}$ has $[\alpha]_D^{30}$ – 120) (ethanol) ; R_f 0.46 (PC, BuOH : AcOH : H_2O :: 4:1:5° and 0.38 (TLC, Benzene : EtOAc :: 1:1) spray vanillin in HCl [6]. λ_{max}^{EtOH} 278 nm. $IR\nu_{max}^{KBr}$ 3450, 2900, 1650, 1540, 1130-1050, 850 and 820 cm^{-1}. Formed acetate with Ac_2O/pyridine m.p. 205° and methyl ether (Me_2SO_4/K_2CO_3) m.p. 180°.

Compound (I) on hydrolysis with 10% ethanolic hydrochloric acid gave an anthocyanidin and a free sugar rhamnose (PC, osazone). The anthocyanidin was identified as cyanidin by colour reactions, paper chromatography $\lambda_{max}^{EtOH-HCl}$ 515 nm and comparison with an authentic sample of cyanidin isolated from the red rose petals[7].

The position of the sugar moiety in the molecule was determined by subjecting the glycoside to catalytic hydrogenation (Pt/H_2)[8] under atmospheric pressure as well as under 15 lbs pressure when no free sugar could be detected. Therefore, the possibility of the sugar linkage at C_4 hydroxyl could be eliminated. The glycoside gave pink colour with *p*-toluene sulphonic acid reagent which showed that hydroxyl at C_5 is free[9]. This was also in conformity with the absorption that in the visible spectrum of the corresponding anthocyanidin a definite shoulder at 450 nm was obtained in addition to the main absorbance at 545 nm. On permethylation[10] and subsequent hydrolysis the glycoside yielded 5,7,3′,4′-tetra-*O*-methyl cyanidin[11] and 2,3,4-tri-*O*-methyl rhamnose indicating that the sugar is linked at C_3. The position of the sugar moiety was further confirmed by conversion of the glycoside into polymeric substance on prolonged acid treatment. The glycoside yielded a polymeric substance whereas the completely methylated glycoside lacked this property showing that sugar is not linked at C_4 of the diol unit[12]. It could thus be inferred that it is a 3-0-glycoside. This is also in agreement with the suggested biogenesis of these compounds[13] which favours position-3 for glycosidation. The methylated glycoside on alkali degradation yielded phloroglucinol dimethyl ether and veratric acid suggesting the attachment of rhamnose at C_3. That rhamnose is present in the pyranose form has been proved by periodate oxidation and nature of the glycosidic linkage as α – by hydrolysis with diastase. Compound(I) is thus leucocyanidin-3-O-α-L(–) rhamnopyranoside.

Compound (II) :

Compound(II) $C_{22}H_{26}O_{11}$ $[\alpha]_D^{2?}$ – 110 (EtOH), R_f 0.54 (PC, BuOH, AcOH : H_2O :: 4:1:5) and 0.42 (tlc, benzene : EtOAc :: 1:1) (spray vanillin in HCl) λ_{max}^{EtOH} 275 nm ν_{max}^{KBr} 3440, 2910, 2880, 1650, 1530, 1450, 1180, 1130-1050, 850, and 825 cm^{-1}. It formed acetate (Ac_2O/Py) m.p. 180° and methyl ether (Me_2SO_4/K_2CO_3) m.p. 160°. On acid hydrolysis it gave rhamnose (PC, osazone) and an anthocyanidin which resembled natural peonidin in its colour reactions and $\lambda_{max}^{EtOH-HCl}$ 540 nm, co-chromatography with a natural sample of peonidin isolated from fresh viola tricolour flowers[14]. Alkali fission of the glycoside yielded phloroglucinol dimethyl ether and veratric acid suggesting the linking of rhamnose either at C_3 or C_4 positions of the leucopeonidin. This was decided in favour of position C_3 by catalytic hydrogenation and polymerisation of the glycoside with mineral acid. On periodate oxidation two moles of periodate were consumed per mole of the glycoside with liberation of one mole of formic acid which suggested the pyranose structure for rhamnose. The glycoside hydrolysed with diastase showing thereby the sugar linkage to be α. This also in conformity with the fact that all the naturally occurring rhamnosides of known structures so far reported have α – configuration[15]. Thus the compound (II) is leucopeonidin-3-O-α-L-(–) rhamnopyranoside.

These two glycoside (I) and (II) have not been reported earlier from any plant sources. The high astringent nature and medicinal uses of the root bark of *C. javanica* is most probably due to the occurrence of compound (I) (0.075%) and compound (II) (0·30%) in high yield.

Acknowledgement

The author is thankful to U.G.C. India for awarding research associateship under special assistance scheme in Chemistry Department of Allahabad University.

References

1. R. D. Tiwari and J. Singh, *Phytochemistry*, 1978, **18**, 906.
2. K. R. Kirtikar and B. D. Basu, Indian Medicinal Plants, Vol. II. p. 877, Leader Press, India (1935).
3. R. D. Tiwari and J. Singh, *Planta Medica*, 1977, **34**, 371, 374.
4. R. D. Tiwari and J. Singh, *Phytochemistry*, 1977, **16**, 1107.
5. R. D. Tiwari and J. Singh, *Phytochemistry*, 1978, **18**, 347.
6. E. C. Bate-Smith, *Biochem. J.*, 1954, **58**, 122.
7. R Willistatter and T. Nolan, *J. Ann.*, 1915, **1**, 408.
8. T.A. Geissmann, The Chemistry of flavonoid compounds, Pergamon Press, 1962, 226.
9. D. J. Roux, *J. Chromatog.*, 1963, **10**, 473.
10. H. E. Khadan and Y. S. Mohammad, *J. Chem. Soc.*, 1958, 3320.
11. S. Agrawal and K. Misra, *Chemica Scripta*, 1977, **12**, 37.
12. D. G. Roux and E. Paulus, *Biochem. J.*, 1962, **83**, 320.
13. J. B. Harborne, *Fortschr. Chem. Org. Naturst.*, 1962, **20**, 165.
14. P. Karrer and G. Neuron, *Helv. Chim. Acta*, 1933, **16**, 292.
15. R. M. Horowitz and B. Gentili, *Tetrahedron*, 1963, **19**, 773.

Polarographic Study of Cd(II)-Acetylacetonate System

(Km.) KRISHNA, S. K. JHA and MUKHTAR SINGH

Chemical Laboratories, Agra College, Agra

Manuscript received 7 April 1979, revised 4 February 1980, accepted 18 March 1980

BRANICA[1,2] and co-workers have undertaken polarographic investigations on acetylacetonate complexes of Cu(II) and Ni(II). The present study deals with the polarography of Cd(II)-acetylacetonate system.

Experimental

Solutions of $CdCl_2$, $NaNO_3$ were prepared from reagent grade chemicals in conductivity water. Acetylacetone was of E. Merck G. R. grade and its aqueous solution was used as ligand. The concentration of Cd(II) in each case was kept at 1×10^{-3} *M*. The concentration of acetylacetonate ion was calculated from the *p*H of the solution and pK value[3-5] of acetylacetone (pK = 8.95).

A manual polarograph (Toshniwal CLO2) with polyflex galvanometer (Toshniwal PL-50) was used. All the measurements were recorded at 30 ± 0.1°. Purified nitrogen gas was passed through the solution to remove the dissolved oxygen. Saturated calomel electrode (S. C. E.) was used as reference electrode. The d.m.e. had the following characteristics (in 0.1 *M* $NaNO_3$, open circuit) : m = 1.673 mg/sec, t = 4.04 sec, $m^{2/3} t^{1/6} = 1.778$ $mg^{2/3}$ $sec^{-1/2}$, $h_{corr} = 63.01$ cm. The number of electrons(n) involved in the reduction process was determined by millicoulometric method of DeVries and Kroon[6]. This gave the value of n = 2 at *p*H 7.

The thermodynamic functions (△G, △H and △S) have been evaluated using relevant equations[7].

Results and Discussion

Polarograms of the solutions containing 1×10^{-3} *M* Cd(II) and 0.1 *M* acetylacetone were taken at different *p*H values. It was observed that the negative shift in $E_{1/2}$ was maximum at *p*H 7 and hence this value was chosen for studying the complex formation between Cd(II) and acetylacetone. The concentration of the ligand was varied from 0.01 to 0.1 *M*. In each case a single well-defined wave appeared. The plots of i_d vs $h_{corr}^{1/2}$ were found to be linear and passing through the origin thereby indicating that the reduction is diffusion-controlled. The plots of log $i/i_d - i$ vs $E_{d.e.}$ were found to be linear with slope of the order of 31 ± 2 mV. This shows that the reduction is reversible. The plot of $E_{1/2}$ against $-\log C_x$ is a straight line. This suggests that Cd(II) forms a single complex with the ligand. The composition and stability constants have been determined by Lingane's[8] method.

The value of co-ordination number, p, comes out to be 1. The composition of the complex is, therefore, $[Cd(Acac.)]^+$. The value of stability-constant has been determined at three different temperatures (20°, 30° and 40°).

The values of stability constant (*β*) and the thermodynamic functions (△G, △H and △S) have been summarised in Table 1.

TABLE 1—VALUES OF LOG *β* AND △G, △H AND △S AT DIFFERENT TEMPERATURES FOR Cd(II)—ACETYLACETONATE SYSTEM
$\mu = 0.1$ ($NaNO_3$)

Temp. °C	log *β*	△H Kcal mole^{-1}	△G Kcal mole^{-1}	△S cal degree^{-1} mole^{-1}
20	4.28	−11.897	−5.74	−0.020
30	3.99	−11.897	−5.44	−0.021
40	3.69	−11.897	−5.12	−0.022

Acknowledgement

Thanks are due to the Principal, Agra College, Agra for providing necessary facilities.

References

1. M. PETEK, L. JEFTIC and M. BRANICA, "Polarography 1964", Vol. I (Proceedings IIIrd Intern. Congr. Southampton) Edited, G. J. Hills, McMillan, London, 1966, p. 491.
2. M. VERGI, B. COSVIC and M. BRANICA, *J. Electroanal. Chem.*, 1969, 3, 22.
3. G. SCHWARZENBACH and K. LUTZ, *Helv. Chim. Acta*, 1940, 23, 1147.
4. W. WALISCH and A. H. RUPPERSBERG, *Ann. Univ. Saraviensis*, 1959, 8, 1.
5. M. L. EIDINOFF, *J. Amer. Chem. Soc.*, 1945, 67, 2072.
6. T. DEVRIES and J. L. KROON, *J. Amer. Chem. Soc.*, 1953, 75, 2484.
7. T. B. TRIVEDI, M. S. PATEL and D. N. VYAS, *J. Indian Chem. Soc.*, 1977, 54, 560.
8. J. J. LINGANE, *Chem. Rev.*, 1941, 29, 1.

Chemical Investigation of Some Mangrove Species : Part VIII. *Lumnitzera racemosa*

S. GHOSH MAJUMDAR and GOURI PATRA

Department of Chemistry, The University of Burdwan, Burdwan 713 104

Manuscript received 6 August 1979, accepted 17 Mach 1980.

A thorough investigation for secondary metabolites of Sundarban mangroves have been undertaken for chemotaxonomic consideration[1-6]. In this present communication triterpenoid constituents of *Lumnitzera racemosa* (Fam. Combrataceae) from two different latitude viz. Kakinada (Lat 20°. NH) and Sundarban (Lat. 16° NH) are described to determine the effect of Insolation upon taxonomic markers.

TABLE 1

Species/Habitat	Portion in Kg.	Compound Isolated					
		A	B	C	D	E	F
L. racemosa Sunderban	Bark 1.75	0.35 g	0.25 g	0.50	0.02	1.00	0.08
	Leaves 3.0	0.50 g	0.15 g	1.50	0.25	0.08	0.10
L. racemosa Kakinada	Bark 3.0	0.70	0.30	0.35	0.05	0.75	0.09
	Leaves 3.0	0.35 g	0.20 g	0.60	0.20	0.60	0.10

A = β-amyrin, B = taraxerol, C = friedelin, D = betulin, E = β-sitosterol, F = triacontanol, g = identified through glc study.

Literature survey showed that the genus Lumnitzera remained unexplored. A species of the genus is a small tree (20-40 ft high), were collected in the month of December from two habitats.

Petroleum extract of dry, powdered bark of the plant from Sundarban was taken up in ether and separated into neutral and acidic fraction as usual procedure[1]. Each of the two fractions were then chromatographed over silica gel G, the former one directly and the latter after esterification with diazomethane. On working up of the acidic fraction it was found to contain a few complex waxy material without any trace of triterpenes.

The neutral fraction on separation over silica gel G furnished the following compounds. Similar compounds with slight variations in yield were isolated (Table 1) from the plant material of Kakinada.

The identity of the constituents was made through m. p., mixed m.p., tlc., co-tlc., glc studies and preparation of some derivatives.

(a) Friedelin m.p. 248° (oxime, m.p. 284°) $[\alpha]_D - 71°$

(b) β-amyrin m.p. 195° (Ret. time 17.7 mins. at 250°, column material : 3% SE 30 on gas chromz 60-80 mesh).

(c) Taraxerol m.p. 268° (Ret. time 20.0 mins. at 250°).

(d) Triacontanol (m.p. 82°).

(e) Betulin m.p. 238 (acetyl, m.p. 212°).

(f) β-sitosterol m.p. 138° $(\alpha)_D - 35°$.

Acknowledgement

We are highly indebted to Sri Prabal Sil and other laboratory colleagues for their constant encouragement and help.

References

1. S. Ghosh Majumdar and Gouri Patra, *J. Indian Chem. Soc.*, 1979, 56, 111.
2. S. Ghosh Majumdar and Gouri Patra, *J. Indian Chem. Soc.*, 1976, 53, 947.
3. S. Ghosh Majumdar and Gouri Patra, *J. Indian Chem. Soc.*, 1976, 53, 1241.
4. S. Ghosh Majumdar and Gouri Patra, *J. Indian Chem. Soc.*, 1978, 55, 414.
5. S. Ghosh Majumdar and Gouri Patra, *J. Indian Chem. Soc.*, 1979, 56, 218.
6. S. Ghosh Majumdar and Gouri Patra, *J. Indian Chem. Soc.*, 1979, 56, 1039.

J. Indian Chem. Soc.,
Vol. LVII, May 1980, pp. 570

Book Review

Solution Chemistry of Surfactants—Vol. I and Vol. II (Plenum Press, New York and London)
Edited by K. L. Mittal

THESE two volumes contain the proceedings of the section on solution chemistry of surfactants of the 52nd Colloid and Surface Science Symposium of the Division of Colloid and Surface Chemistry held at Knoxville, Tennessee, June 12-14, 1978, under the auspices of the American Chemical Society.

Altogether 49 papers by 108 contributors from 19 countries are included in these volumes. The papers are reproduced directly from type scripts.

The contributions represent a good coverage of many a theoretical as well as practical aspects of solution chemistry of surfactants.

The varied topics covered by the articles include ; thermodynamics and kinetics of micellisation in aqueous solution, aggregation of surfactants in aqueous and nonaqueous media, mixed micelles, solubilisation, micellar catalysis and inhibition, microemulsion, tertiary oil recovery, liquid crystals, surface rheological properties, phase stability, adsorption at various interfaces along with a number of inter and multidisciplinary aspects of solution chemistry of surfactants.

The articles differ substantially in scope. Some of them present overview of a broad field while others are conventional research papers which include experimental details. The overview articles although useful, informative and well documented deal with work and results, a large portion of which has been published previously and some repetitions have inevitably crept in. The standards of some of the papers are not high enough to grace the occasion.

Recent energy crisis and the prospects of tertiary oil recovery have given a strong impetus to research on microemulsion and the articles covering this area give a good account of the current state of research activities. Some of the technological aspects of micellar chemistry have been described in a few papers. The overview papers dealing with the application and use of micellar systems in analytical and electrochemical investigations are useful and important contributions. The ever increasing investigations in micellar media including photochemical studies which has assumed great importance because of the possibility of light energy storage in micellar systems, are well represented. But the biological aspects of the subject have not received appropriate attention. The topic certainly deserves better coverage at this stage of the subject.

A noteworthy feature of the volumes is that the articles are well documented and quite a number of references are made to papers published as recently as 1978.

Individual research workers may not find all of the volumes of value and feel to add to their private collection but they contain many interesting and useful contributions to some of which the same workers will be substantially interested.

The volumes will make an asset to any library as a very useful reference source and help keep pace with the information explosion in the field concerned.

A. R. Das

AUTHOR INDEX

J. Indian Chem. Soc.,
Vol. LVII, June 1980, pp. 571-575

Metal Complexes of Thiopolycarboxylic Acid (III) : Co(II), Ni(II) and Cu(II) Complexes with Methylenebisthioacetic Acid and Their Pyridine Derivatives

S. K. TIWARI, (MRS.) S. JAIN, A. KUMAR and K. C. TIWARI

Chemical Laboratories, Z. H. College of Engineering and Technology, Aligarh Muslim University, Aligarh-202 001 (India)

Manuscript received 27 February 1978, revised 5 May 1979, accepted 19 May 1980

Complexes of Co(II), Ni(II) and Cu(II) with methylenebisthioacetic acid and their pyridine derivatives were prepared. Structures have been characterised on the basis of magnetic moment, electronic and infrared spectral studies. The results are in agreement with the octahedral arrangement of the coordination sphere of the metal ions studied.

IN continuation of our work on metal complexes of thiopolycarboxylic acids [1,2], the present paper extends our studies to the preparation and characterisation of methylenebisthioacetic acid (MBTAA-H_2), $CH_2(SCH_2COOH)_2$ complexes with Co(II), Ni(II) and Cu(II) and their pyridine derivatives. MBTAA-H_2 containing two thio and two carboxylic groups and nitrogen from pyridine as potential donors, may, therefore, combine in various polydentate modes.

Experimental

Chemicals : MBTAA-H_2 of 99.5% purity (Evans Chemetics, New York) was used without further purification. All other chemicals used were of chemically pure grade.

Preparation of the metal Complexes : MBTAA-H_2 form solid complexes with Co, Ni and Cu ions. These compounds were prepared by the general method described below using the metal chlorides for Co(II) and Ni(II) and nitrate for Cu(II), with reference to the Co(II)-MBTAA-H_2 complex.

25 ml aqueous solution of cobalt chloride was added to an equimolar solution of MBTAA-H_2 (75 ml) in alcohol. A few drops of concentrated solution of NaOH were then added and the resulting mixture were refluxed for seven hours. A violet coloured solid was then separated out on cooling in ice cold water. It was filtered and washed with water, alcohol and ether and dried in vacuum over $CaCl_2$.

Complexes of Ni(II) and Cu(II), in green and greenish yellow colour respectively were prepared by the similar method.

Pyridine Derivatives : Pyridine-MBTAA-H_2 complexes of Co(II) in dark violet, Ni(II) in dark green and Cu(II) in dark bluish green colour were prepared by the similar method as described above, for Co(II)-MBTAA-H_2, after mixing MBTAA-H_2 and pyridine, in appropriate quantity, before adding metal and NaOH solutions.

All these complexes were slightly soluble in hot water and common organic solvents.

Physical Measurements : The instruments and methods have been given previously[1].

Results and Discussion

Results are given in Table 1. The decomposition temperatures which range between 160° and 298° indicate that the complexes are thermally quite stable. The molar conductance of these complexes in DMSO indicates the non-electrolytic nature of these complexes (Table 2).

Co(II) Complexes : The observed magnetic moments of 4.97 and 5.22 B.M. (Table 2) for Co(MBTAA) and Co(MBTAA).2Py respectively are in agreement with the generally accepted values 4.80-5.60 B.M. for high-spin octahedral Co(II) complexes[3], suggests that these complexes are octahedral. The electronic spectra (Table 3) of Co(MBTAA) complex is consistent with the octahedral or tetragonal arrangement of the ligand. Since the complex formed has D_4h symmetry, the electronic spectra can, therefore, be interpreted in terms of metal ion surrounded by a weak ligand field of octahedral microsymmetry. The octahedral Co(II) complexes, generally, exhibit three spin-allowed bands corresponding to the transitions $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ (ν_1), $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ (ν_2) and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) in order of increasing energies in the absorption spectra. However, the transition $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ (ν_2) may or may not be observed because of the weakness and proximity to a strong (ν_3) transition. The observed electronic spectra (Table 3) consists of two main bands. The

TABLE 1—CHEMICAL ANALYSIS OF MBTAA-H_2 AND THEIR PYRIDINE COMPLEXES

Compound	%Metal		%Carbon		%Hydrogen		%Sulphur		%Nitrogen		Decomposition Temperature °C
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	
$Co(C_5H_6S_2O_4)$	23.28	23.34	23.72	23.76	2.39	2.35	25.33	25.38	—	—	270
$Ni(C_5H_6S_2O_4)$	23.21	23.30	23.74	23.71	2.39	2.32	25.23	25.16	—	—	265
$Cu(C_5H_6S_2O_4)2H_2O$	21.62	21.64	20.44	20.38	3.43	3.34	21.82	21.75	—	—	160
$Co(C_5H_6S_2O_4)2Py$	13.53	13.48	46.89	46.82	3.70	3.76	14.72	14.78	6.43	6.39	298
$Ni(C_5H_6S_2O_4)2Py$	13.49	13.39	46.92	46.88	3.70	3.78	14.73	14.80	6.44	6.38	280
$Cu(C_5H_6S_2O_4)2Py$	14.37	14.45	46.40	46.48	3.66	3.72	14.57	14.68	6 36	6.28	200

TABLE 2—MAGNETIC MOMENT AND CONDUCTANCE MEASUREMENTS OF MBTAA-H_2 AND THEIR PYRIDINE COMPLEXES

Compound	Temp. (°K)	$\chi_M \times 10^6$ uncorr. (c.g.s.)	$\chi_M \times 10^6$ corr. (c.g.s)	μ_{eff} B.M.	Molar conductance ohm^{-1} cm^2 mole^{-1}
$Co(C_5H_6S_2O_4)$	298.0	10185.78	10276.60	4.97	2.1
$Ni(C_5H_6S_2O_4)$	298.0	4206.24	4297.26	3.21	2.2
$Cu(C_5H_6S_2O_4).2H_2O$	298 0	1413.16	1530.18	1.95	2.1
$Co(C_5H_6S_2O_4).2Py$	298.0	11122.12	11325.58	5.22	6.8
$Ni(C_5H_6S_2O_4).2Py$	298.0	4558.42	4761.88	3 38	7.3
$Cu(C_5H_6S_2O_4).2Py$	298.0	1214.86	1418.32	1.85	6.0

TABLE 3—DIFFUSE REFLECTANCE SPECTRA AND LIGAND FIELD PARAMETERS OF MBTAA-H_2 AND THEIR PYRIDINE COMPLEXES

Compounds	Bands kK	Assignments	D_q cm^{-1}	Racah's Parameter (B) cm^{-1}	L.F.S.E. K cal/mole	ν_2/ν_1	B^*	Ep term separation cm^{-1}	$\left(\frac{992}{1041}\right)B_{Ni^{2+}}$
$Co(C_5H_6S_2O_4)$	7.80(ν_1)	$^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)$	848	858	19.33	2.05	0.883	12872	859
	16.00(ν_2)	$\rightarrow{}^4A_{2g}(F)$							
	19.60(ν_3)	$\rightarrow{}^4T_{1g}(P)$							
$Ni(C_5H_6S_2O_4)$	8.40(ν_1)	$^3A_{2g}(F)\rightarrow{}^3T_{2g}(F)$	840	920	28.72	1.66	0.884	13800	—
	14.00(ν_2)	$\rightarrow{}^3T_{1g}(F)$							
	25.00(ν_3)	$\rightarrow{}^3T_{1g}(P)$							
$Cu(C_5H_6S_2O_4).2H_2O$	13.00	$^2E_g \rightarrow{}^2T_{2g}$	1300	—	22.28	—	—	—	—
$Co(C_5H_6S_2O_4).2Py$	8.00(ν_1)	$^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)$	870	873	19.83	2.07	0.900	13090	871
	16.00(ν_2)	$\rightarrow{}^4A_{2g}(F)$							
	20.00(ν_3)	$\rightarrow{}^4T_{1g}(P)$							
$Ni(C_5H_6S_2O_4).2Py$	8.60(ν_1)	$^3A_2(F)\rightarrow{}^3T_{2g}(F)$	860	933	29.41	1.67	0.896	14000	—
	14.40(ν_2)	$\rightarrow{}^3T_{1g}(F)$							
	25.40(ν_3)	$\rightarrow{}^3T_{1g}(P)$							
$Cu(C_5H_6S_2O_4).2Py$	14.00	$^2E_g \rightarrow{}^2T_{2g}$	1400	—	23.94	—	—	—	—

lowest energy band at 7.80 kK is, therefore, assigned as (ν_1) and the strong band at 19.60 kK as (ν_3). A third weak band observed at 16.00 kK is, however, assumed as (ν_2) transition. These observed bands are quite similar[4] to $[Co(H_2O)_6]^{2+}$. To resolve the position of (ν_2) transition, on the basis of octahedral symmetry, the ligand field parameters were calculated (Table 3) by the use of semi-empirical equations[5]. The calculated value of (ν_2), 16.28 kK using the relation[6] $\nu_2 = \nu_1 + 10$ Dq, is in good agreement with the observed band at 16.00 kK. Further, Lever[7] has shown that in case of an octahedral Co(II) complex the (ν_2) transition must have an energy approximately twice but not greater than 2.2 times that of (ν_1) transition. The observed ratio (ν_2/ν_1) as 2.05 also supports the assignment of the band at 16.00 kK to (ν_2) corresponding to the transition $^4T_{1g}(F)\rightarrow{}^4A_{2g}$.

In case of Co(MBTAA).2Py complex the observed electronic spectra consists of three main bands at 8.00 kK (ν_1) ; 16.60 kK (ν_2) and 20.00 kK (ν_3). These bands also correspond to other octahedral Co(II) complexes. The calculated value of ν_2 at 16.70 kK and observed ratio ν_2/ν_1 as 2.07 supports the octahedral structure of the complex. As discussed above the ligand field parameters (Table 3) were calculated on the basis of octahedral symmetry.

Ni(II) Complex : Our observed magnetic moment values of 3.21 and 3.38 B.M. for Ni(MBTAA) and Ni(MBTAA).2Py respectively (Table 2) clearly indicate the octahedral[8] nature of these complexes.

The electronic spectra of the Ni(MBTAA) complex (Table 3) indicates a octahedral or tetragonal arrangement of the ligand. Although the complex formally has D_4h symmetry, the electronic spectrum in the range of 8.00-30.00 kK and magnetic moment value are typically of octahedrally coordinated Ni(II). The observed energies of the spin-allowed transitions $^3A_{2g} \rightarrow ^3T_{2g}$ (ν_1) at 8.40 kK, $^3A_{2g} \rightarrow ^3T_{1g}(F)$ (ν_2) at 14.00 kK and $^3A_{2g} \rightarrow ^3T_{1g}(P)$ (ν_3) at 25.00 kK agree well with those predicted from Liehr and Ballhausen[9] energy leval diagram for Ni(II) in a ligand field of octahedral symmetry. These bands are also very similar to those of nickel aquate[10] $[Ni(H_2O)_6]^{2+}$. The ligand field parameter, 10 Dq was taken equal to the observed energy of the first triplet transition (ν_1) and the Racah parameter, B was calculated by the substitution of (ν_1), (ν_2) and (ν_3) band energies in the secular equation[11]. The calculation includes the mutual interaction between the T_{1g} levels but ignores spin-orbit coupling. The observed separation, 11.00 kK of (ν_2) and (ν_3) bands compared with the calculated value[11] of 11.04, on the basis of octahedral symmetry, further supports that the tetragonal distortion is rather small and the complex remains practically octahedral. Furthermore, our value of 1.66 for ratio (ν_2/ν_1) is in accord with the commonly reported value of 1.60-1.70 for Ni(II) complex of octahedral symmetry and indicates a strong T_{1g} levels interaction[12].

The observed electronic spectra of Ni(MBTAA). 2Py complex also consists of three bands (Table 3) at 8.60 kK (ν_1), 14.40 kK (ν_2) and 25.40 kK (ν_3) as compared with Ni(MBTAA) complex. The observed separation, 11.00 kK of (ν_2) and (ν_3) band with the calculated value of 11.19 kK and the value of 1.67 for ratio (ν_2/ν_1) support that the Ni(MBTAA).2Py complex is also octahedral.

In these complexes the reduction of B after multiplying by B $\left(\frac{Co^{2+}}{Ni^{2+}}\right)$ gaseous, the so-called nephelauxetic effect[13], seems to be more effective for Co(II) ion than for Ni(II) ion.

Cu(II) Complexes : Majority of Cu(II) complexes show magnetic moment values[14] of 1.75-2.20 B.M. near the spin only value of 1.73 B.M. indicating the absence of any appreciable spin coupling between unpaired electrons belonging to different copper atoms. The magnetic moment of tetrahedral complexes are generally higher than the square planar or octahedral Cu(II) complexes[3,15]. On the other hand, some complexes like Cu(II) carboxylates[16,17] and the so-called tri-coordinated Cu(II) complexes[18] show a subnormal magnetic moment<1.73 B.M. but not in all carboxyl group bridged polymers like Cu(II) benzoate trihydrate[19] which has a magnetic moment of 1.87 B.M. The observed magnetic moment values of 1.95 and 1.85 B.M. for Cu(MBTAA) and Cu(MBTAA).2Py respectively (Table 2) excludes strong spin-spin pairing but does not exclude a polymeric structure.

The electronic spectra of an octahedrally coordinated Cu(II) complex should normally exhibit one absorption band due to $^2E_g \rightarrow ^2T_{2g}$ transition. State ^2E_g is highly susceptible to John Teller distortion and no Cu(II) complex should have a regular octahedral symmetry. The observed spectrum of Cu(MBTAA) and Cu(MBTAA).2Py shows only one broad band (Table 3) at 13.00 kK and 14.00 kK respectively. The complex being formally of D_4h symmetry excludes a square planar form because a square planar copper(II) shows two bands of nearly equal intensity at about 15.00 kK corresponding to the transitions[20-22] $^2B_{1g} \rightarrow ^2A_{1g}$ and $^2B_{1g} \rightarrow ^2E_g$ respectively. Therefore, the observed bands are identified as d-d band $^2E_g \rightarrow ^2T_{2g}$ of octahedral Cu(II) ion.

Infrared Spectra : The infrared spectra of the ligand and its complexes were recorded in the region 4000-200 cm^{-1}. The important bands and their tentative assignments (Table 4) were obtained with reference to the spectra of other carboxylate complexes as well as those of thio and amino acid complexes[23-26]. The (C–S) stretching band at 730 cm^{-1} of the ligand on complexation was found to shift to lower frequency indicating the coordination through sulphur similar to analogous systems of thiopolycarboxylic metal chelates[1,2,24]. The metal sulphur stretching bands of the first transition metals have been reported to occur over a wide range of wave number[14]. The bands of monothio or dithio diketonates occur at about 350 cm^{-1} but in case of thiourea adducts[27] bands range from 205-298 cm^{-1}. It is, therefore, quite reasonable to assume that the observed bands in the region 245-265 cm^{-1}, in these complexes, are due to ν(M–S) vibrations. The symmetric COO^- stretching band in the ligand also shifted to lower frequency. The antisymmetric (COO) stretching band on complexation also shifted to lower frequencies in the region 1580-1590 cm^{-1} except in Cu(II) complex and Δ(COO) was always less than 220 cm^{-1} indicates that both carboxyl groups act as bidentate. The bridging carboxylic groups of metal carboxylate complexes also show an absorption in this region. Further, the OH deformation band at 810 cm^{-1} in the ligand disappears on complexation as the ionization of the carboxylic group is envisaged in coordination. It is, therefore, concluded that coordination takes place through both sulphur and carboxylate groups. The observed strong band at 3340 cm^{-1} indicates the presence of water molecule in Cu(II) complex and the second observed

TABLE 4—TENTATIVE ASSIGNMENTS OF IMPORTANT INFRARED BANDS OF MBTAA-H_2 AND THEIR PYRIDINE COMPLEXES

(L – H_2)	Co(L)	Ni(L)	Cu(L)2H_2O	Co(L).2Py	Ni(L)2Py	Cu(L)2Py	Tentative Assignments
1710(s)	1590(s)	1590(s)	1650(s)	1710(s)	1710(s)	1710(s)	(COO) asym
1410(s)	1400(s)	1400(s)	1405(m)	1400(s)	1405(m)	1410(s)	(COO) sym
800	190	190(s)	245	240	250	245	(COO)
810(m)	—	—	—	—	—	—	– OH deformation
795(s)	790(s)	790(m)	785(m)	790(m)	785(m)	790(m)	(O – C = O)
780(s)	710(m)	710(m)	710(s)	705(m)	705(m)	710(s)	(C – S)
—	—	—	—	510(m)	550(m)	520(m)	(M – N)
—	250(s)	260(m)	260(m)	245(s)	265(m)	250(s)	(M – S)

L – H_2 = MBTAA-H_2($C_6H_6S_2O_4$), s = strong, m = medium.

band at 940 cm^{-1} was, however, assigned to coordinated water molecules which was further supported by thermogravimetric analysis indicating the loss of one molecule of water at 145° (weight loss = 6.00%, theoretical = 6.130%) and another at 160° (weight loss = 13.00%, theoretical = 12.30%). Thus Cu(II) complex is six coordinated and the two coordination positions are occupied by two water molecules. On the other hand, in case of, anhydrous Co(II) and Ni(II) complexes, the magnetic and spectral data indicate that these complexes are octahedral.

Pyridine Complexes : The magnetic moment and electronic spectra of these complexes indicate that the central metal ion is six coordinated, with high-spin essentially octahedral configuration. For this two most likely possibilities are : (a) Coordination via two N- and two S-atoms and two O-atoms of the (COO) groups, or (b) Coordination via two -N atoms and four O-atoms of (COO) groups. A comparison of (MBTAA-H_2) and their complexes with pyridine (Table 4) helps to distinguish between these two possibilities.

The (C – S) stretching band on complexation was found to shift to lower frequency indicating the coordination through sulphur. This was further supported by metal sulphur band observed in the region of 225-260 cm^{-1}. The position of the bands of antisymmetric stretching vibrations of the carboxylic groups as well as the difference of the antisymmetric and symmetric vibrations, Δ(COO) always higher than 220 cm^{-1} indicate the covalent character of the carboxyl-metal bond[28,29] indicate that MBTAA reacts as a tetradentate. The coordination of carboxylic oxygen was further supported by the disappearance of – OH deformation band at 810 cm^{-1} in free ligand. The ligand MBTTA-H_2 as well as its Co(II), Ni(II) and Cu(II) complexes have no absorption band in the region 400-600 cm^{-1} whereas the (M – N) stretching band in the chelated Co(II), Ni(II) and Cu(II) complexes usually appears in the region 400-600 cm^{-1} [30,31]. Thus the observed bands in the region 510-550 cm^{-1} in all pyridine complexes are due to (M – N) stretching vibrations which lie in plain and out of plain deformation coordination of pyridine to the metal ion.

The above facts suggest that pyridine complexes are octahedral and their coordination sphere is completed via two N- and two S- atoms and two O-atoms of (COO) groups.

Acknowledgement

The authors are grateful to M/s Evans Chemetics Inc., New York for the gift sample of MBTAA – H_2. The authors are also grateful to Prof. W. Rahman, Head, Chemistry Department for providing research facilities.

References

1. A. KUMAR, S. JAIN and S. K. TIWARI, *J. Inorg. Nuclear Chem.*, 1975, **37**, 2439.
2. S. K. TIWARI, A. KUMAR, S. JAIN and N. P. PARASHAR, *J. Indian Chem. Soc.*, 1976, **53**, 872.
3. B. N. FIGGIS and J. LEWIS, *Prog. Inorg. Chem.*, 1964, **6**, 37.
4. A. LUDI and W. FEIKNECHT, *Helv. Chim. Acta*, 1963, **46**, 2226.
5. J. REEDIJK, W. L. DRIENSSEN and W. L. GROENEVELD, *Rec. Trav. Chim.*, 1969, **88**, 1095.
6. C. J. BALLHAUSAN, 'Introduction to Ligand Field Theory', McGraw-Hill, New York, 1962.
7. A. B. P. LEVER, *J. Chem. Soc.*, A 1967, 2041.
8. R. S. NYHOLM ; *Chem. Revs.*, 1953, **53**, 263.
9. A. D. LIEHR and C. J. BALLHAUSEN, *Ann. Phys.*, 1959, **6**, 134.
10. C. K. JORGENSEN, *Acta. Chem. Scand.*, 1955, **9**, 1362.
11. O. BOSTRUP and C. K. JORGENSEN, *Acta. Chem. Scand.*, 1957, **11**, 1223.
12. A. B. P. LEVER, *Coord. Chem. Rev.*, 1968, **3**, 119.
13. A. D. LIEHR, *J. Phys. Chem.*, 1963, **67**, 1314.
14. F. A. COTTON and G. WILKINSEN, 'Advance Inorganic Chemistry' 2nd Ed., Interscience Publisher, New York, (N. Y.) 1966.
15. B. N. FIGGIS and C. M. HARRIS, *J. Chem. Soc.*, 1959, 855.
16. R. L. MARTIN and H. WATERMAN, *J. Chem. Soc.*, 1959, 1359, 2960.
17. M. KISHITA, M. INOVE and M. KUBO, *Inorg. Chem.*, 1964, **3**, 237.
18. M. KISHITA, M. KUBO, Y. KURODA and Y. MUTO, *Austral. J. Chem.*, 1963, **16**, 7.
19. M. INOVE, T. KISHITA and S. KUBO Nippon ; *Nagaku Zassi*, 1963, **84**, 759.

20. J. P. FACKLER, Jr., F. A. COTTON and D. W. BARNUM, *J. Amer. Chem. Soc.*, 1963, **82**, 97.

21. F. A. COTTON and J. J. WISE, *J. Amer Chem. Soc.*, 1966, **88**, 3451 ; *Inorg. Chem.*, 1967, **6**, 917.

22. B. N. FIGGIS, 'Introduction to Ligand Fields', Interscience Publisher, New York (N. Y.) 1966.

23. C. A. MCAULIFFI and W. D. PERRY, *J. Chem. Soc.* A, 1969, 634.

24. K. NAKAMOTO, 'Infrared Spectra of Inorganic and Coordination Compounds', John Wiley & Sons, New York, 1963.

25. S. E. WIBERLEY, S. C. BUNCE and W. H. BANNER, *Analyt. Chem.*, 1960, **32**, 217.

26. C. G. BARRALLOUGH, R. L. MARTIN and I. M. STEWART, *Austral. J Chem.*, 1969, **22**, 891.

27. D. M. ADAM and J. B. CORNELL, *J. Chem. Soc.* A, 1967, 884.

28. E. K. NAKOMOTO and P. J. MCCARTHY, 'Spectroscopy and Structure of Metal Chelate Compounds', Wiley, New York, 1968.

29. D. T. SAWYER, *Ann. N. Y. Acad. Sci.*, 1960, **88**, 307.

30. K. NAMURA, *J. Chem. Soc.* (Japan), 1959, **80**, 1848.

31. K. UENO and A. E. MARTELL, *J. Phys. Chem.*, 1958, **59**, 998 ; 1956, **60**, 1270.

J. Indian Chem. Soc.,
Vol. LVII, June 1980, pp. 576-579

Potentiometric Studies on Mixed Ligand Complexes of Gallium(III), Taking NTA as Primary Ligand and Some Aliphatic Carboxylic Acids as Secondary Ligands

K. R. DIXIT and K. N. MUNSHI*

Department of Chemistry, Nagpur University, Nagpur-10

Manuscript received 20 January 1979, revised 8 June 1979, accepted 19 May 1980

Potentiometric studies on some mixed ligand complexes of Ga(III) are reported. Nitrilotriacetic acid (NTA) was used as primary ligand whereas, malic acid, maleic acid, malonic acid, succinic acid, oxalic acid and itaconic acid were employed as secondary ligands. Log K^{MA}_{MAL} was evaluated, using modified form of Irving and Rossotti's method. The stability constant values were found to be in the order, malonic acid≃maleic acid>malic acid>oxalic acid>succinic acid>itaconic acid. Thermodynamic parameters, e.g. ΔG°, ΔH° and ΔS° have also been evaluated. Results obtained are correlated on the basis of steric and structural characteristics of the chelates.

IN the last decade several reports have come on the study of mixed ligand complexes of heavier metals[1-4], but no attempt appears to have been made on the study of mixed ligand complexes of Ga(III) except for a spectrophotometric report[6]. The present communication describes the results obtained in the potentiometric studies of some mixed ligand complexes of Ga(III). Nitrilotriacetic acid (NTA) was used as primary ligand (A), whereas malic acid (MA), maleic acid (MAE), succinic acid (SUC), malonic acid (MLA), oxalic acid (OXA) and itaconic acid (ITCA) were employed as secondary ligands (L). The study of binary complexes of these primary as well as secondary ligands with Ga(III) has been reported by earlier workers[7-9]. The modified method of Irving and Rossotti[10] is applied to determine that log K^{MA}_{MAL}. All studies were performed at a constant ionic strength of 0.2*M* ($NaClO_4$) and at three different temperature, viz. 15°, 30° and 45°. The thermodynamic parameters ΔG°, ΔH° and ΔS° were also evaluated.

Experimental

Material : A stock solution of $Ga(NO_3)_3 \cdot xH_2O$(BDH) was prepared in a known quantity of perchloric acid to prevent the hydrolysis of metal ion. The metal content was estimated by the precipitation of Ga(III) as 8-hydroxyquinolinate[11]. Stock solution of 0.01*M* NTA, 0.2*M* perchloric acid, 2.0*M* sodium perchlorate and 0.02*M* solutions of secondary ligands were prepared in double distilled water and estimated potentiometrically. Carbonate free sodium hydroxide was prepared by standard method[12].

Expanded scale *p*H meter (accuracy ±0.02 *p*H unit) of ECIL fitted with a glass-calomel assembly was used to measure [H⁺] of solution. Saturated calomel electrode was connected externally by means of an agar-agar salt bridge saturated with KNO_3 to prevent the formation of chloro-complex. Temperature were maintained with an accuracy of ±0.1° by the help of U-10 thermostat. All the experiments were done in an inert atmosphere created by bubbling nitrogen through the solution throughout the course of titration.

Procedure : Four mixtures were prepared as follows :

Mixture A : $HClO_4$ ($2.37\times10^{-3}M$) ; *Mixture B :* $HClO_4$ ($2.37\times10^{-3}M$)+secondary ligand ($1.0\times10^{-3}M$) ; *Mixture C :* $HClO_4$ ($2.37\times10^{-3}M$) +metal solution ($1.0\times10^{-3}M$)+primary ligand (1.0×10^{-3}) ; *Mixture D :* $HClO_4$ ($2.37\times10^{-3}M$) +secondary ligand ($1.0\times10^{-3}M$)+primary ligand ($1.0\times10^{-3}M$)+metal solution ($1.0\times10^{-3}M$). These mixtures were prepared in such a manner that the concentration of common ingredients were identical in each case. An appropriate amount of neutral $NaClO_4$ was added to maintain the desired ionic strength. The total volume of all systems were kept identical by adding double distilled water. The ratio of M : A : L was kept 1 : 1 : 1. A graph between *p*H-meter reading and volume of alkali added was plotted. The four titration curves so obtained were refered to as : (A) Acid curve, (B) Secondary ligand curve, (C) Primary complexation curve and (D) Mixed ligand complexation curve.

Results and Discussion

Practical Proton-Ligand Stability Constants of Secondary Ligands :

The values of $\bar{n}_A$ at various *p*H-meter readings were calculated from acid and ligand titration

* For Correspondence

curves for secondary ligands. The equation (1) as used by Irving and Rossotti was employed :

$$\bar{n}_A = [YT^{\circ}_{CL} + \frac{(V'-V'')(N+E^{\circ})}{(V^{\circ}+V')}]/T^{\circ}_{CL} \quad \ldots (1)$$

where V' and V'' denotes the volume of alkali added to reach the same value of pH in the titration of acid and ligand respectively ; T°_{CL} is the total ligand concentration ; Y is the total number of replaceable protons attached to ligand ; N is the normality of alkali used and E° the initial strength of acid in the system.

A graph is plotted between $\bar{n}_A$ against pH and practical proton-ligand stability constants were evaluated by (a) the method of interpolation at half $\bar{n}_A$ values and (b) the method of interpolation at various $\bar{n}_A$ values. The values obtained at various temperature and at $\mu=0.2M$ ($NaClO_4$) for all these secondary ligands are summarized in Table 1.

Metal-Ligand Stability Constants : In the present case the formation constants have been obtained by plotting $\bar{n}$ against pL. The values of $\bar{n}$, the average number of ligand molecule attached per metal ion is calculated from equation (2) :

$$\bar{n} = \frac{(V'''-V'')(N+E^{\circ})}{(V^{\circ}+V')\bar{n}_A T^{\circ}_{CM}} \quad \ldots (2)$$

where T°_{CM} denotes the total concentration of metal ion present in solution, V''' and V'' are the difference in volume of alkali added between curve D and C ; B and A respectively to attain the same pH-meter reading. $\bar{n}_A$ is the average number of protons attached to secondary ligand at same pH. The free ligand exponent, pL has been calculated from equation (3) :

$$pL = \log \frac{\sum_{n=0}^{n=j} \beta^H_n (1/\text{antilog}\,[H^+])^n}{T^{\circ}_{CL} - \bar{n}T^{\circ}_{CM}} \cdot \frac{(V^{\circ}+V'''')}{V^{\circ}} \quad \ldots (3)$$

where β^H_n is the overall practical proton ligand stability constant and V'''' is the volume of alkali required for curve D at the same pH.

From the titration curves (Fig. 1 as an example) it is revealed that the primary complex formation (Curve C) takes place at very low pH and the calculations show that it is stable upto pH 7.5. Primary complex curve C and mixed complex curve D overlap each other at lower pH values indicating that in this range, where primary ligand combines with Ga(III), attachment of secondary ligand does not take place. The mixed complex curve D, separates from primary complex curve C at pH 2.8 due to self dissociation of secondary ligand. After pH 3.0 mixed complex curve shows the indication

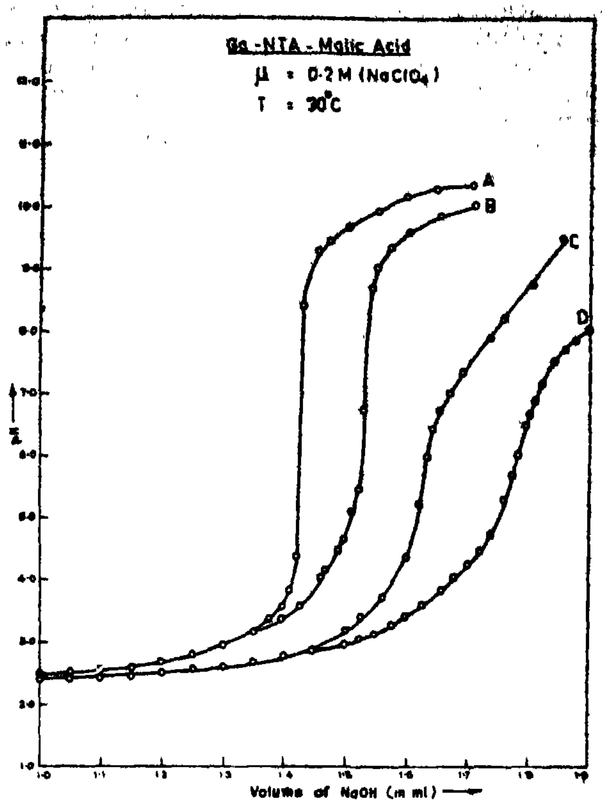


Fig. 1. Titration Curve for Ga(III)-NTA-MA mixed ligand Complex at 30° and $\mu=0.2M$.

Curve A : $2.37\times10^{-3}M$ perchloric acid ;

Curve B : $2.37\times10^{-3}M$ perchloric acid, $1.0\times10^{-3}M$. MA ;

Curve C : $2.37\times10^{-3}M$ perchloric acid, $1.0\times10^{-3}M$. Ga(III) and $1.0\times10^{-3}M$. NTA ;

Curve D : $2.37\times10^{-3}M$ perchloric acid, $1.0\times10^{-3}M$, MA, $1.0\times10^{-3}M$ NTA and $1.0\times10^{-3}M$. Ga(III).

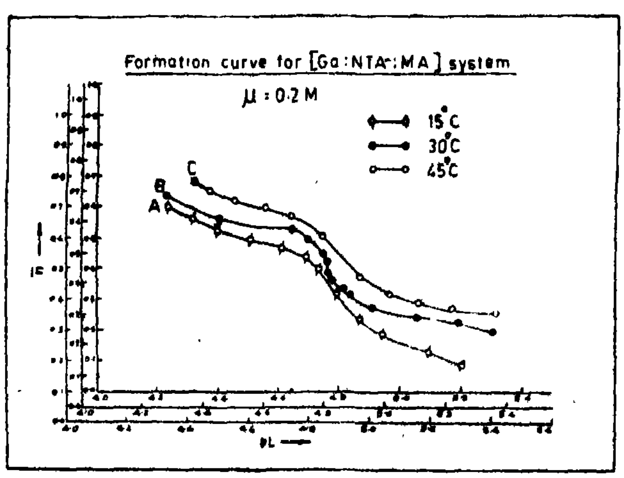


Fig. 2. Formation Curve for [Ga(III)-NTA-MA] at different temperatures.

of attachment of secondary ligand with gallium. Since the dissociation of [Ga(NTA)] does not take place in the range of dissociation of secondary ligand, it can be considered that secondary ligand combines with [Ga(III)-NTA]. In presence of secondary ligand the formation of [Ga-NTA-$(OH)_n$] is also suppressed.

The values of $\bar{n}$ were calculated taking into consideration the difference from curve C and D, (V‴) from which the difference of curve A and B (V″) is subtracted at various *p*H values. A typical plot of $\bar{n}$ against pL for [Ga-NTA-MA] has been shown in Fig. 2. The values of log K^{MA}_{MAL} have been evaluated using the method (A) interpolation of various $\bar{n}$ values and (B) interpolation of half $\bar{n}$ value. They are summarized in Table 1. The error limits are ±0.05 log unit. It is however necessary to clear at this point that the above constants calculated here are really not overall mixed ligand stability constants but a step constant for the reaction :

$$MA + L \rightleftharpoons MAL$$

where A is the primary ligand and L is the secondary ligand.

TABLE 1—PRACTICAL PROTON LIGAND STABILITY CONSTANTS OF LIGANDS AND METAL-LIGAND STABILITY CONSTANTS OF Ga(III)-MIXED LIGAND COMPLEXES
$\mu = 0.2M(NaClO_4)$

Ligand	pK/log K	Temperature 15°		30°		45°	
		A	B	A	B	A	B
MA	log K^H_1	4.64	4.66	4.60	4.59	4.56	4.54
	log K^H_2	3.44	3.45	3.40	3.42	3.34	3.36
	log β^H	8.08	8.11	8.00	8.01	7.90	7.90
MAE	log K^H_1	5.72	5.71	5.68	5.70	5.62	5.64
	log K^H_2	3.08	3.10	3.00	3.03	3.02	3.01
	log β^H	8.80	8.81	8.68	8.71	8.64	8.65
MLA	log K^H_1	5.15	5.13	5.12	5.10	5.08	5.07
	log K^H_2	3.42	3.41	3.38	3.39	3.32	3.32
	log β^H	8.57	8.54	8.50	8.41	8.40	8.39
SUC	log K^H_1	5.22	5.21	5.16	5.18	5.10	5.09
	log K^H_2	4.13	4.15	4.10	4.07	4.08	4.07
	log β^H	9.35	9.36	9.26	9.25	9.18	9.16
OXA	log K^H_1	3.93	3.92	3.88	3.85	3.82	3.80
	log K^H_2	1.86	1.85	1.80	1.82	1.74	1.75
	log β^H	5.79	5.77	5.68	5.67	5.56	5.55
ITCA	log K^H_1	5.28	5.28	5.22	5.25	5.18	5.21
	log K^H_2	3.92	3.91	3.90	3.87	3.88	3.86
	log β^H	9.20	9.19	9.12	9.12	9.06	9.07
[Ga-NTA-MA]	log K	4.85	4.86	4.80	4.78	4.74	4.69
[Ga-NTA-MAE]	log K	5.56	5.58	5.52	5.53	5.49	5.43
[Ga-NTA-MLA]	log K	5.55	5.56	5.53	5.49	5.50	5.45
[Ga-NTA-SUC]	log K	4.37	4.40	4.35	4.33	4.32	4.25
[Ga-NTA-OXA]	log K	4.59	4.61	4.56	4.55	4.52	4.48
[Ga-NTA-ITCA]	log K	3.34	3.38	2.26	3.29	3.18	3.19

Similar titration curves are obtained for other systems and results obtained are also summarized in Table 1.

Thermodynamic Parameters : The values of the change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) have been calculated at three different temperatures and at a constant ionic strength of 0.2 *M* $NaClO_4$, with the help of temperature coefficient and Gibb's Helmoholtz equation[18]. The value of free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) calculated at three different temperature are summarized in Table 2.

TABLE 2—THERMODYNAMIC FUNCTIONS OF Ga(III) MIXED LIGAND COMPLEXES
$\mu = 0.2M(NaClO_4)$

System	Temp.	ΔG°K cal/mol	ΔH°K cal/mol	ΔS°e.s.u.
[Ga-NTA-MA]	15°	−6.39	−2.40	+13.8
	30°	−6.61		
	45°	−6.81		
[Ga-NTA-MAE]	15°	−7.34	−1.72	+19.4
	30°	−7.63		
	45°	−7.93		
[Ga-NTA-MLA]	15°	−7.33	−1.71	+19.9
	30°	−7.61		
	45°	−8.09		
[Ga-NTA-SUC]	15°	−6.06	−1.70	+15.1
	30°	−6.29		
	45°	−6.51		
[Ga-NTA-OXA]	15°	−5.79	−2.16	+13.0
	30°	−6.00		
	45°	−6.51		
[Ga-NTA-ITCA]	15°	−4.40	−2.7	+ 6.0
	30°	−4.55		
	45°	−4.64		

Discussion

The data in Table 2 provides a summary of the results obtained in the present work. The stability constants were found to be in the order MLA ⇌MAE>MA>OXA>SUC>ITCA. This order may be justified on the basis of (A) ring size of chelate and (B) the structural and donor characteristics of ligand molecule.

MLA forms 6-membered chelate ring, OXA forms 5-membered while SUC, ITCA, MA and MAE form seven membered chelate rings. So the expected trend from Bayer's strain theory will be MLA>OXA>SUC, ITCA, MA and MAE. The extra stability of MAE and MA chelate can be attributed to the structural characteristics of the ligands. The presence of conjugate double bond in the MAE chelate ring increases the stability of chelate by exocyclic conjugation while the OH-group present in MA increases the tendency of ligand to give proton at early *p*H because of its electron-withdrawing tendency. The lower stability of OXA chelate with respect to MA and MAE chelate might also be described due to the high stability of oxalic acid

anion because of resonance, which results in the reduction of complexing behaviour of oxalic acid.

The order of stability constants in 7-membered chelate is MAE>MA>SUC>ITCA. The high stability of MAE and MA chelate is already described while the lower stability of ITCA chelate in comparison to succinic acid chelate might be due to the presence of methyl group in ITCA ligand. This group is electron donating whereby the liberation of proton becomes difficult and the complexing tendencies of the ligand decreases.

The above trend in stability constant were further confirmed by the values of ΔG° obtained during the course of investigation.

References

1. K. N. Munshi and T. H. Mhaske, *J. Indian Chem. Soc.*, 1976, **53**, 11.
2. K. N. Munshi and T. H. Mhaske, *Indian J. Chem.*, 1976, **14(A)**, 421.
3. K. N. Munshi and A. M. Pujari, *J. Indian Chem. Soc.*, 1977, **54**, 681.
4. D. N. Shelke and D. V. Jahagirdar, *J. Indian Chem. Soc.*, 1978, **55**, 545.
5. S. P. Singh, H. S. Verma and J. P. Tandon, *J. Indian Chem. Soc.*, 1978, **55**, 539.
6. A. P. Zharkov, F. Ya. Kulba and V. N. Volkov, *Zh. Neorg. Khim.*, 1977, **22(5)**, 1223 (Russ).
7. R. S. Ambulkar, Ph. D. Thesis, Nagpur University, Nagpur (1976).
8. R. S. Ambulkar and K. N. Munshi, *Indian J. Chem.*, 1976, **14**, 424.
9. E. A. Biryuk and R. V. Ravitskaya, *Z. Anal. Khim.*, 1971, **26**, 1752.
10. H. M. Irving and H. S. Rossotti, *J. Chem. Soc.*, 1954, 2904.
11. L. Erdey, "Gravimetric Analysis" Inst. Ser. of monographs analyt. Chem. Vol. 7 (Pergamon, New York, 1965).
12. A. I. Vogel, "Quantitative Inorganic Analysis" (Longmann Publication, 1971).
13. K. B. Yatsimirskii and V. P. Vasi'l'ev, "Instability Cons'ants of Complex Compounds" (Pergamon, New York, 1960).

J. Indian Chem. Soc.,
Vol. LVII, June 1980, pp. 580-582

Determination of Stability Constants of 2-Hydroxy-1-Naphthalidene-*p*-N-Dimethylaminoaniline Complexes with Pr^{3+}, Nd^{3+}, Gd^{3+} and Dy^{3+}

M. S. MAYADEO and V. P. DHAKAPPA

Department of Chemistry, Ramnarain Ruia College, Bombay-400 019

Manuscript received 21 January 1979, revised 29 January 1980, accepted 19 May 1980

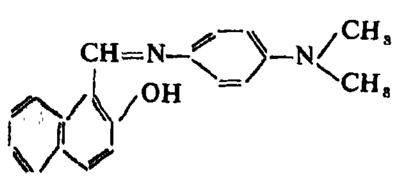
Potentiometric studies have been carried out on metal complexes of Pr^{3+}, Nd^{3+}, Gd^{3+} and Dy^{3+}, with 2-hydroxy-1-naphthalidene-p-N-dimethylaminoaniline. The dissociation constants (pK_1 and pK_2) of the reagent and the formation constants of its metal complexes have been determined by Bjerrum's method at 25±0.1° and at ionic strength 0.1*M* in 75 : 25 per cent (v/v) dioxan-water medium. The order of stability constants of the chelates is found to be $Dy^{3+}>Pr^{3+}>Gd^{3+}>Nd^{3+}$. The validity of Born's relation was examined by studying the plot of Z^2/r vs log K values of the rare earth complexes of the ligand.

IN the present communication the successive stability constants of the complexes of 2-hydroxy-1-naphthalidene-*p*-N-dimethylaminoaniline with various trivalent metal ions have been determined potentiometrically following the Calvin-Bjerrum *p*H titration technique as adopted by Irving and Rossotti[1].

The Corning Model 12, a precision research *p*H meter with a combined glass electrode and a calomel reference electrode was used for *p*H measurements. Both electrodes dip into the titration mixture, without vitiating any of the results. The meter has an arrangement for normal and expanded scale. The changes in *p*H can be measured with an accuracy of 0.005 *p*H unit.

Experimental

The ligand, 2-hydroxy-1-naphthalidene-*p*-N-dimethylaminoaniline was prepared by dissolving 10 gm of 2-hydroxy-1-naphthaldehyde (Fluka) in 50 ml of absolute ethanol. To this was added equimolar quantity of *p*-N-dimethylaminoaniline and the reaction mixture was refluxed on a water bath for half an hour. After cooling, the solution was filtered to get the crude product, which was repeatedly crystallised from ethanol to get analytically pure compound with m.p. 168° (observed). The structural formula of the ligand is—



The dioxan used for experimental work was purified by the method described by Vogel[2]. Distilled water redistilled over alkaline potassium permanganate was used throughout the investigation.

The medium of titration was 75 : 25 per cent dioxan-water (v/v) mixture. Sodium perchlorate was added to maintain a constant ionic strength. The titrations were carried out in an inert atmosphere by bubbling the oxygen free nitrogen gas through the solutions. The free acid, the free acid plus the ligand and the mixture of metal ion containing the acid plus the ligand were titrated against standard carbonate free sodium hydroxide. The solutions of metal perchlorates were prepared using metal carbonate of pure quality (Fluka) and A. R. grade perchloric acid. All these were standardised complexometrically[3] by EDTA titrations. All measurements were carried out at 25±0.1°.

The following solutions were titrated potentiometrically against standard carbonate free sodium hydroxide (1.025 *M*), solution.

(i) 5 ml of (0.16 *M*) $HClO_4$+5 ml of (0.64 *M*) $NaClO_4$+30 ml of dioxan.

(ii) 5 ml of (0.16 *M*) $HClO_4$+5 ml of (0.64 *M*) $NaClO_4$+requisite amount of reagent accurately weighed to give 0.004 *M* reagent concentration in the final solution+30 ml of dioxan.

(iii) 5 ml of (0.64 *M*) $NaClO_4$+5 ml of metal perchlorate (0.008 *M*) in (0.16 *M*) $HClO_4$+the requisite amount of the reagent accurately weighed to give 0.004 *M* reagent concentration in the final solution+30 ml of dioxan.

The data obtained from above titrations are presented in Fig. 1.

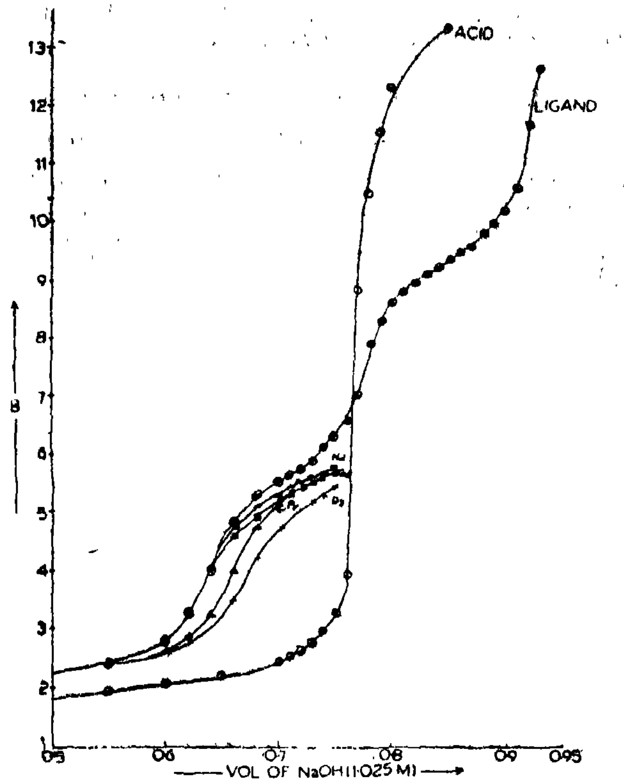


Fig. 1. Titration curves of 2-hydroxy-1-naphthalidene-p-N-dimethylaminoaniline.

The experimental method of Irving and Rossotti[1] was applied to find out the values of $\bar{n}$ and pL. The titrations were performed in duplicate to test the reproducibility.

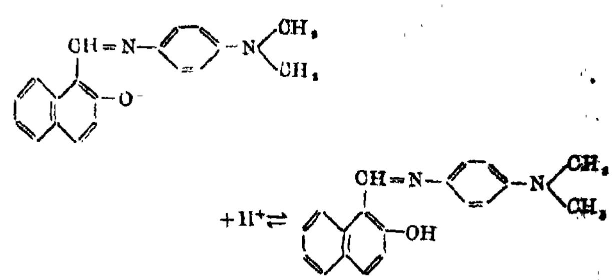
Results and Discussion

It may be stated here that the reagent does not undergo hydrolysis under the experimental conditions described. This was indicated by rapid attainment of equilibrium during the titration and by the absence of any significant drift in pH even after one hour. This has also been confirmed by T.L.C. taken from time to time of a sample titration mixture.

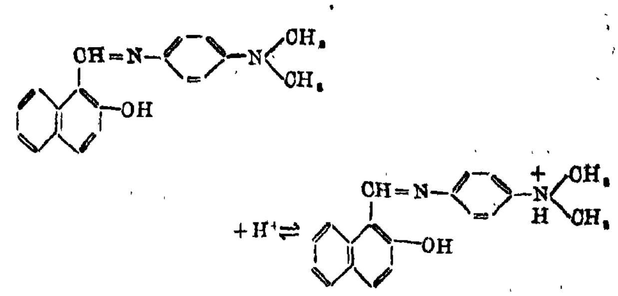
In the ligand it is the phenolic (OH) group which takes part in the complex formation and the proton is replaced from it by metal ions during chelation. Since only one proton per ligand molecule is liberated during complexation, 'Y', the number of dissociable protons attached to each ligand molecule is one.

From the titration curves (Fig. 1) using the solutions (i) and (ii), $\bar{n}_A$ values at various 'B' values (pH meter readings) were calculated and a curve between 'B' and the corresponding $\bar{n}_A$ values was plotted. The formation curve extends over a range $0.15 < \bar{n}_A < 1.8$ and is wavelike. The value of pK_1^H which corresponds to phenolic 'H' was evaluated from the half-integral point at $\bar{n}_A = 0.5$ while that of pK_2^H which corresponds to the association of protonated nitrogen was obtained at $\bar{n}_A = 1.5$.

The formation of LH corresponds to the reaction



while the reaction leading to the formation of LH_2^+ can be



The protonation of the nitrogen of —CH=N— (imino nitrogen) does not take place in the range of pH under study as this nitrogen is less basic as compared to the nitrogen of $-N(CH_3)_2$ group.

The plots of $\log\left[\frac{\bar{n}_A}{1-\bar{n}_A}\right]$ vs B and $\log\left[\frac{(2-\bar{n}_A)}{(\bar{n}_A-1)}\right]$ against B were also drawn. From the former pK_1^H was evaluated and from the latter pK_2^H was evaluated. The values agree quite well with those obtained by the half-integral method.

From the titration curves using solutions (ii) and (iii), $\bar{n}$ and pL values were calculated. The $\bar{n}$ values were plotted against the corresponding pL values to get the formation curves of the metal complexion equilibria (Fig. 2). From these formation curves, the values of stability constants $\log K_1$ were calculated which correspond to pL values at $\bar{n} = 0.5$. The plot of $\log\left[\frac{\bar{n}}{(1-\bar{n})}\right]$ against pL was also drawn for these systems. The values of $\log K_1$ evaluated from these plots agree quite well with those obtained by half-integral method.

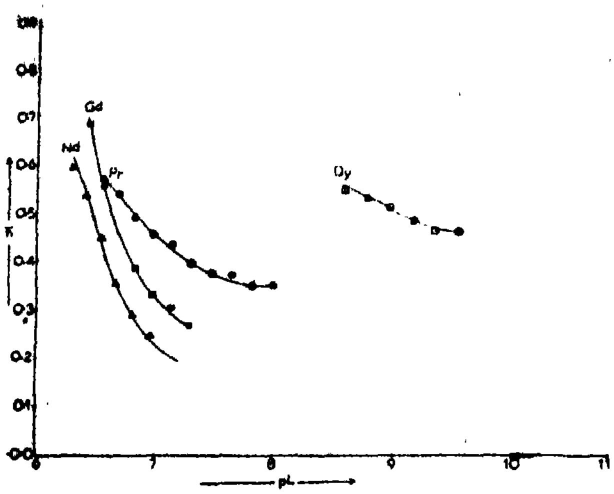


Fig. 2. Metal ligand systems of 2-hydroxy-1-naphthalidene-p-N-dimethylaminoaniline.

The most representative values are recorded in Table 1. The order of stability of the trivalent metal chelates was found to be $Dy^{3+}>Pr^{3+}>Gd^{3+}>Nd^{3+}$.

TABLE 1—STEPWISE STABILITY CONSTANTS OF VARIOUS COMPLEXES*

t=25°C μ=0.1

Cations	H^+	Pr^{3+}	Nd^{3+}	Gd^{3+}	Dy^{3+}
log K_1	9.82	6.82	6.48	6.63	9.02
log K_2	5.37	—	—	—	—

* For proton association (H^+), K_1 and K_2 corresponds to the species LH and LH_2^+ respectively, while for metal ions K_1 corresponds to the species ML_1.

The second step formation constants for metal chelates could not be evaluated because of precipitation of metal ions probably due to metal ion hydrolysis.

Rare earths normally form ionic compounds. The possibility of covalent interaction, however, cannot be completely excluded as reported in the case of acetylacetone chelates of rare earths[4].

If the bonds are ionic, the Born relation $E=Z^2/2r\left(1-\frac{1}{D}\right)$ should hold for the energy change on complexation of a gaseous ion of charge 'Z' and radius 'r' *in a medium of dielectric constant* 'D'. Since the stability constant is related directly to this energy, the log K values should increase linearly with Z^2/r.

The plots of Z^2/r vs log K_1 values of the rare earth complexes do not exhibit any linear increase of log K_1 with increase in Z^2/r. The probable explanation of non-linearity could be that the assumption about ionic character of metal-ligand bond on which the *linear* relation is based is not valid. The other probable causes are (i) coordination number of metal ion greater than six, and (ii) steric factor.

Acknowledgement

The authors wish to record their sincere thanks to Dr. D. G. Vartak, B. A. R. C., Bombay, for the valuable suggestions and to Dr. R. A. Kulkarni, Principal, Ramnarain Ruia College, Bombay, for his kind and continuous encouragement in accomplishing this work.

References

1. H. M. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.*, 1954, 2904.
2. A. I. VOGEL, A Text Book of Practical Organic Chemistry, III Edition, Longmans, p. 177.
3. H. A. FLASCHKA, 'EDTA Titrations', Pergamon Press, N. Y., p. 78.
4. T. D. MOELLER, *Chem. Rev.*, 1965, 65, 1.

J. Indian Chem. Soc.,
Vol. LVII, June 1980, pp. 583-585

Determination of Dissociation Constants of Some Amino Acids : Part II—by Spectrophotometric Method

LEELA PARDESHI and R. A. BHOBE*

Department of Chemistry, Marathwada University, Aurangabad, Maharashtra, India

Manuscript received 18 May 1979, revised 26 November 1979, accepted 4 March 1980

The authors have used Ernst and Menashi's method of ultraviolet spectrophotometry and have evaluated the pK_1 and pK_2 values of Cysteine (1.94, 8.82), Tryptophane (2.30, 9.44), Phenyl alanine (1.79, 9.16) and Tyrosine (2.18, 9.18) respectively. These compare favourably well with those found potentiometrically.

IT is fairly well known that amino acids either absorb in the shorter wave length or long wavelength region, especially to a greater or lesser extent in the ultraviolet range. The main advantage of determining dissociation constants by spectrophotometric method over other methods, such as potentiometry or titrimetry, was that the optical measurements made at very low concentrations of the order of 10^{-4} mole/l were as accurate as made at higher concentrations and were most reliable.

Experimental

The amino acids chosen for this study namely Cysteine (α-amino β-mercapto propionic acid), Phenylalanine (α-amino β-phenyl propionic acid), Tryptophane (α-amino β-indole propionic acid) and Tyrosin (α-amino β [p-hydroxy phenyl] propionic acid were obtained from British Drug House Ltd, Poole, England. The spectral results were recorded on Unicam SP 500 spectrophotometer previously checked for wavelengths by didymium glass absorption peaks as also by checking λ_{max} of spec-pure solvents such as ethanol, acetone, methanol and chloroform. All results were obtained in an air-conditioned room (25°) with a thermostatic arrangement on silica cuvettes (25°±0.2°). Suitable wavelengths, in the region 200-300 nm, were so chosen that the difference between the extinction coefficients of the undissociated and charged species was large enough for the determination of dissociation constants by the method of Ernst and Menashi[1]. For this, the absorption curves of the respective amino acids were traced in neutral, aqueous, 0.68 $HClO_4$, 0.036 NaOH and 0.55 *N* NaOH media. For comparison, the dissociation constants of the acids were determined on Leed and Northrup *p*H meter by titrating 50 ml of 0.01 *M* acid against 0.1 *N* KOH and 0.1 *N* HCl respectively for the two *p*K values of the amino acid.

Theoretical Background :

The theory given below is a combined contribution of Silverthorn and Curtis[3], Stearns and Wheland[4] and Ernst and Menashi[1].

If the acid H_2A dissociated as

$$H_2A \rightleftharpoons H_2A^{-1} + H^+$$
$$HA \rightleftharpoons H^+ + A^{-2} \text{ then}$$

$$K_1 = \frac{h\gamma_1^2(HA^{-1})}{(H_2A)} \quad \ldots (1)$$

and

$$K_2 = \frac{h\gamma_2^2(A^{-2})}{(HA^{-1})} \quad \ldots (2)$$

where K_1 and K_2 are the dissociation constants, γ_1, γ_2 are the activity coefficients and h is simply (H^+).

Lambert-Beer Law gives :

$$D = (H_2A)E_1 + (HA^-)E_2 + (A^{2-})E_3 \quad \ldots (3)$$

where E_1, E_2, E_3 are the molar extinction coefficients for the species in brackets and by the same logic,

$$D_1 = E_1C, \quad D_2 = E_2C, \quad D_3 = E_3C \quad \ldots (4)$$

where D = optical density. Ang[6] has shown that the above equations can be cast into a form (by reasonable assumptions) :

$$\frac{1}{D_1 - D} = \frac{1}{D_1 - D_2} + \frac{h\gamma^2}{K_1(D_1 - D_2)} \quad \ldots (5)$$

Hence the plot of $\frac{1}{(D_1 - D)}$ vs $h\gamma^2$ should give

* Senior author to whom all correspondence should be addressed.

K_1 since the intercept gives the value of $1/D_1-D_2$ automatically. The activity coefficient γ can be calculated on the lines of Davies[6] and Butler[6a] by using the expression :

$$-\log_{10}\gamma\pm=0.5\,Z^2\frac{\sqrt{I}}{1+\sqrt{I}}-0.3I \quad \ldots \quad (6)$$

where $I=h+b \quad \ldots \quad (7)$

b being the stoichiometric concentration of NaOH added (as in the present case), $h=(H^+)$ and I = ionic strength, Z being the charge.

Results and Discussion

For the purpose of final calculation of K_2 the expression used is a modification of expression (5) above and is written as :

$$\frac{1}{D_1-D}=\frac{1}{D_2-D_1}+\frac{h\gamma_2}{K_2(D_2-D_1)} \quad \ldots \quad (8)$$

$$\text{i.e.}=\frac{1}{D_2-D_1}+\frac{kw\gamma_2}{K_2(D_2-D_1)}f l^2(OH^-) \quad \ldots \quad (9)$$

where K_2 is the second dissociation constant of the amino acid, kw, ionic product for H_2O (1.008×10^{-14}) and γ_2 is the activity coefficient of the species. The factor b, as defined above (expression 7), is used in evaluating (OH^-) as :

$$[OH^-]=b-\left[1+\frac{D-D_1}{D_2-D_1}\right]\times C \quad \ldots \quad (10)$$

where C is the concentration of amino acid.

It will be seen from the expression above that the values of K_1 and D_2 can be easily determined only if $h\gamma_1^2$ can be evaluated. Since h is defined by the expression :

$$h=a+\left[\frac{m(D-D_1)}{D-D_2}\right] \quad \ldots \quad (11)$$

where $a=(ClO_4)^-$ and is the stoichiometric concentration of $HClO_4$ added and $m=(H_2A)+(HA^-)+(A^{2-}) \quad \ldots \quad (12)$

knowledge of D_2 is essential and for its evaluation from the graph, h is simply taken to be the concentration of $HClO_4$ as a first approximation.

It need not be stressed that in order to determine K_2, known concentrations of NaOH are to be added to the amino acid solution. The present series of acids are specially chosen because they could form $5.55\times10^{-3}M$; $1.08\times10^{-2}M$; $5.64\times10^{-3}M$ and $1.50\times10^{-2}M$ aqueous solution with ease.

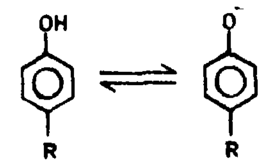
Although all amino acids absorb to a lesser or greater extent in uv region, the amino acids studied by the present authors absorb[7] in the given range of 220 to 300 nm. Beaven and Holiday[10] have worked in this field extensively and have found that the molecular extinction coefficients (Em) of tryptophane, tyrosin in alkaline media are much higher than those in acidic ones. The trend followed in the present series (Table 1) is

TABLE 1—THE RELEVANT DATA OF λ_{max} (nm) AND Em VALUES OF THE AMINO ACIDS IN NEUTRAL ALKALINE AND ACIDIC MEDIA

Amino Acid	λ_{max} in media (Em values in paranthesis) H_2O	0.036N NaOH	0.55N NaOH	0.68N $HClO_4$
Tyrosine	273 (155.71)	279 (162.10)	281 (165.78)	275 (152.87)
Cysteine	250 (69.44)	254 (75.92)	258 (81.48)	250 (67.19)
DL Tryptophane	274 (193.2)	283 (202.1)	283 (206.9)	279 (184.2)
DL Phenylalanine	265 (74.66)	266 (78.12)	267 (79.29)	266 (72.91)

Em alkaline≥Em neutral≥Em acidic, unmistakably in all the acids studied which bears out the observation made by Beaven and Holiday[8].

Strenstrom and Reinhard[9] make an identical observation, specially in case of tyrosin, and assign the sensitive absorption in the alkaline medium as due to the ionization of the phenolic group in this acid as :



Formageot and Schnek[10] confirm this observation by stating that in the region 290.0 to 310 nm, the phenoxide ion of Tyrosin absorbs very strongly whereas the phenolic group of the acid reacts less strongly. The observation of the present authors in the case of tyrosin is, Em neutral $\sim1.0\times10^3$ whereas Em alkaline $\sim1.6\times10^3$ which holds good in other cases too, and lends excellent support to their observation.

The data given in Table 1 lists the absorption maxima and Em values for the amino acids studied in neutral, 0.036 N NaOH, 0.55 N NaOH and 0.68N $HClO_4$ media. The K_1 values have been listed in Table 2 and K_2 values are obtained from the expressions :

$$K_1K_2(D_1-D)+K_1h\gamma_2(D_1-D_2)+h^2\gamma_1^2\gamma_2(D_1-D)=0 \quad \ldots \quad (13)$$

$$\text{and } K_2=(D_1-D_2)+h\gamma_2(D_1-D_2)=0 \quad \ldots \quad (14)$$

TABLE 2—pK_1 AND pK_2 VALUES OF THE AUTHORS SPECTROPHOTOMETRICALLY AND POTENTIOMETRICALLY AND OTHER VALUES (a) AND (b)

Amino Acid / pK values	U. V. Spectrophotometry (Present work)		Potentiometry (Present work)		pK values by other workers (a) and (b)			
	pK_1	pK_2	pK_1	pK_2	$pK_1^{(a)}$	$pK_2^{(a)}$	$pK_1^{(b)}$	$pK_2^{(b)}$
Cysteine	1.94	8.82	1.92	8.90	1.96	8.18	1.96	8.88
Tryptophane	2.30	9.44	2.42	9.42	2.38	9.39	2.20	9.55
Phenylalanine	1.79	9.16	1.81	9.26	1.83	9.13	2.04	9.31
Tyrosine	2.18	9.18	2.20	9.14	2.20	9.11	2.20	9.19

(a) Cohn and Edsall[12];
(b) A. Albert[13].

All these have been set out in Table 2 (as pK values) along with the standard potentiometric values of pK_1 and pK_2 with acidic and basic titration as obtained by authors and other workers in the field. Thus the present authors have usefully employed the method spelled out by Ernst and Menashi[1] though the initiation of this method by Benesch and Benesch[11] is gratefully acknowledged by them.

Acknowledgement

One of the authors (Leela Pardeshi) is grateful to Dr. K. A. Thakar, Professor and Head, Chemistry Department for facilities extended to her for conduct of the post-doctoral work.

References

1. Z. L. ERNST and J. MENASHI, *Trans. Faraday Soc.* 1963, **59**, 230.
2. Operating, Maintenance and Service Manual, SP 600 Spectrophotometer, p. 4.
3. R. W. SILVERTHORN and J. A. CURTIS, *Metal and Alloys*, 1942, 15245.
4. R. S. STEARNS and G. W. WHELAND, *J. Amer. Chem. Soc.*, 1947, **69**, 2025.
5. P. ANG, *J. Phys. Chem.*, 1958, **62**, 1109.
6. C. W. DAVIES, Ion Association, Butt rworths, London, 1962, p. 41.
6(a). J. N. BUTLER, "Ionic Equilibrium", Addison—Wesley Pub., London, 1964, p. 441.
7. Organic Chemistry, Vol. I, John Wiley & Sons, New York, 1942, p. 241.
8. G. H. BEAVEN and E. R. HOLIDAY, Advances in Protein Chemistry, 1952, 7, 319.
9. R. STEENSTROM and A. REINHARD, *J. Biol. Chem.*, 1925, **66**, 819.
10. C. FROMAGEOT and W. SCHNEK, *Biochem. Biophys. Acta*, 1925, **6**, 819.
11. R. BENESCH and R. BENESCH, *J. Amer. Chem. Soc.*, 1955, **77**, 5877.
12. E. J. COHN and J. T. EDSALL, Proteins, Amino Acids and Peptides, "Reinhold Publishing Corporation, New York, 1943.
13. A. ALBERT, *Biochem. J.*, 1950, **47**, 531.

J. Indian Chem. Soc.,
Vol. LVII, June 1980, pp. 586-590

Chromatographic Separations of Certain Metallic Ions Using Solutions of Certain Schiff-Bases in the Mobile Phase

(Km.) P. KHANNA and P. B. CHAKRAWARTI*

Chemical Laboratories, M.L.B. College, Bhopal-462 008

Manuscript received 17 August 1979, accepted 30 December 1979

Chromatographic separations of certain closely resembling metallic ions, which are involved in various important special alloys have been effected over plain and impregnated papers, thin layers of silica gel and cellulose. Solutions of certain Schiff-bases derived from Vanillin in pure and mixed solvents were used for irrigating plain papers and thin layers spotted with the metallic ions, while a series of polar and nonpolar solvents constitute the mobile phase in case of the impregnated papers. The results obtained with these techniques have been compared with those obtained using paper electrophoresis and have been discussed in the light of the phenomenon of the coordination.

THE involvement of the phenomenon of coordination (or complex formation) in chromatographic separations of metallic ions has been established well, not only for the detection of the ion on paper but also for the development of the chromatogram. In recent years an increasing emphasis has been laid on the use of complexing agents in the mobile phase for effecting differential migration of the ions on paper, as complex formation has been suggested as one of the important phenomena responsible for the adsorption and desorption of the metallic ions on paper[1]. This has also encouraged the use of impregnated papers. In the present work an attempt has been made to study the separations of some of the closely resembling metallic ions, important not only from the point of view of qualitative separations, but also with reference to the compositions of various important special alloys used in the high tensile-steels for supersonic jets, rockets and missiles which present difficult separations.[2,3] The mobile phase used for these separations consists in solutions of Schiff-bases derived from vanillin and sulphanilic acid (VS), anthranilic acid (VA) and hydrazine (VH) in pure and mixed solvents. While the stationary phase involved plain and impregnated (with a 2% ethanol solution of VS, VA or VH) papers and thin layers of cellulose and silica gel. The results obtained with these techniques have been compared with those obtained with paper electrophoresis and discussed on the basis of phenomenon of coordination.

Experimental

Whatman No 1 *filter paper discs* of diameter 11 cm were used for paper chromatographic separations using Rutter's technique of radial development[4], with the wicks (width 2 mm and length 2-3 cm) having tapering free ends.

For the preparation of *impregnated papers*, these discs were soaked in an alcoholic solutions (2% w/v) of VA or VH [some of the discs were soaked in an aqueous solution of VH (2% w/v)] and then dried in an inert atmosphere at room temperature and stored in polythene bags.

For TLC, Atlantis, TLC apparatus model ATLC-2, was used. Thin layers of cellulose (Chromatographic, BDH) and silica gel (German, Chromatographic) (Thickness 0.5 mm) were prepared on glass plates of $8\frac{1}{2}'' \times 8\frac{1}{2}''$ with the applicator supplied with the kit. The plates were dried at room temperature and then activated at 110° for 2 hrs. The chromatograms were developed in the air-tight glass chamber supplied with the kit.

AR grade soluble salts of Cu(II), Co(II), Ni(II), Fe(II), Fe(III), Cr(III), Cr(VI), Mn(II), Pb(II), Al(III), Zn(II), Cd(II), Hg(II), Bi(III), Sn(II), Be(II), Mg(II), Ca(II), Sr(II), Ba(II), Ag(I), Ce(IV), Mo(VI), W(VI), V(IV), Ti(IV) and Pt(IV) were dissolved in doubly distilled water to get stock solutions (0.1*M*) of the metallic ions.

For the irrigation of the plain papers or the thin layers, 0.01*M* alcoholic solutions of VA, VH and VS were used. The effect of the presence of acid in the solvent on the mobilities of the ions was studied by mixing 1*M* HCl or acetic acid with the alcoholic solutions of VA or VH in the ratio (volume to volume basis), VA/VH : acid, 5 : 1, 10 : 1, 20 : 1, and 25 : 1. The solvents used with the impregnated papers involve chromatographic pure organic solvents, ethanol, dimethyl ketone, dioxane, ethyl acetate and chloroform. The effect of the presence of acid in the mobile phase was studied by mixing ethanol with 1*M* HCl or acetic acid in the ratio (v/v) 10 : 1 (the ratio which gave better separations with TLC

studies). The effect of the impregnation on the mobilities of the metallic ions was also studied and compared with the use of the standard solvent mixture[5], acetic acid, ethyl acetate and HCl(2*M*) in the ratio (v/v) 9 : 9 : 2 for the separation of Cu(II) Co(II) and Ni(II) ions.

For paper-electrophoretic studies, horizontal paper electrophoresis tank and the accompanying power supply were used, with the Whatman No 1 filter paper strips of 300 × 40 mm size.

The electrolyte solutions used for the study were 0.01*M* alcoholic solutions of VA and VH, 0.01*M* aqueous solution of sodium salt of VS, VA-pyridine buffer of *p*H 6.03 ; VS-pyridine buffer of *p*H 5.90 and VH-acetic acid (2*M*) mixture (10 : 1) of *p*H 3.95.

Spotting of the metallic ions was done by micropipette of 1 ml (~0.02 ml per drop). After the spots had been dried, development was carried out by irrigating with the required solvent for the required time, in air-tight chambers, previously saturated with the vapours of the solvent concerned.

The paper discs, strips or the Tl-plates (after marking the solvent front in case of paper chromatography and TLC) were dried at room temperature and the positions of the metallic ions were detected using suitable spray reagents[8]. For the calculations of Rf-values (ratio of movement of the ion and the solvent) the distance from the centre of the spot to the starting point was taken, while for electrophoretic studies the distance moved by the ion from the point of the application has been taken. The results obtained are given in Tables 1-4 ; while the separational possibilities in binary, ternary and polynary mixtures are recorded in Tables I-III.

TABLE 1—Rf-VALUES OF CERTAIN METALLIC IONS ON PAPER DISCS

Paper = Whatman No. 1 Time—2 hrs

Metallic Ions	Rf-values × 100 Solvents A	B	C	Metallic Ions	Rf-values × 100 Solvents A	B	C
Be(II)	77	78	87	Al(III)	78	76	100
Mg(II)	74	68	100	Fe(III)	81	81	100
Ca(II)	72	66	91	Cr(III)	83	83	100
Sr(II)	83	97	87	Ce(IV)	51	81	95
Ba(II)	50	97	79	Pt(IV)	97	60	92
Fe(II)	25	21	100	As(III)	38	35	90
Co(II)	26	17	90	V(IV)	61	56	100
Ni(II)	73	71	100	U(VI)	81	82	100
Cu(II)	45	30	100	Zr(IV)	83	81	100
Mn(II)	23	31	100	Mo(VI)	31	56	98
Pb(II)	53	50	88	W(VI)	65	67	100
Zn(II)	17	72	100	Cr(VI)	65	65	97
Hg(II)	85	87	82				
Bi(II)	84	88	100				
Cd(II)	71	70	98				
Sn(II)	94	90	92				

TABLE 3—Rf-VALUES OF METALLIC IONS ON FILTER PAPER STRIPS BY DESCENDING METHOD

Paper = Whatman No. 1 Time—2 hrs

Metallic Ions	Rf-values × 100 A	B	C
Mg(II)	78··	79	89
Al(III)	82··	86	80··
Mn(II)	53··	88	90
Zn(II)	80·	69	62··
Fe(II)	59··	78··	90
Fe(III)	55··	49.8··	81
Cr(III)	0	0	0
Zr(IV)	0	0	0
V(IV)	89·+	75·	87··
Mo(VI)	29+	47·	48·
W(VI)	72	55··	53··
Ti(IV)	96	86	93
U(VI)	41··	56.8··	86··
Co(II)	84··	58.4··	90
Ni(II)	55··	87.9··	89
Cu(II)	80.9·	64.1··	92

· Diffused.
·· Broad Band.
+ Tailings.

TABLE 2—Rf-VALUES OF CERTAIN METALLIC IONS ON THE LAYERS OF SILICA GEL AND CELLULOSE

Activation time—2 hrs. at 110°C ; Run time—1 hr. at 30°C

Metallic Ions	Silica gel ; Rf-values × 100 Solvents B	A	D	E	F	H	J	L
Cu(II)	11.0·	11.8·	59	60·	45.3	10.8	79·	64
Ni(II)	35+	16.5·	71+	48+	41.4+	76	67	75
Co(II)	7.6·	5.5·	63	50	42.1+	76.8+	67	71
Fe(II)	—	—	—	—	—	—	—	—
Mo(VI)	9.1	6.2·	57+	50+	40.6·	7.9·	57+	25·
V(IV)	14	10.2·	50	45·	42.9·	32.6·	61	25·
Zr(IV)	20·	0	0	0	0	0	62·	14
Ti(IV)	16	7	0	55	51.5	7.2	66	35
Fe(III)	9.1·	8.6·	61	31·	25.7·	33.3+	60	15
Al(III)	16	5.5·	54	46+	31.2+	3.6·	55·	7·
Mg(II)	11·	28.3+	76	66	35.1	4.3	61·	23

Metallic Ions	Cellulose ; Rf-values × 100 Solvents A	C	D	E	G	H	I	J	K	M
Cu(II)	2.6·	100·	21.8·	28.9·	64·	7.4·	28.1·	28·	60.4	17.8·
Ni(II)	30.6·	87·	62.7+	43.5	70+	38.5·	42.2·	41.8·	57·	38.8·
Co(II)	3.3·	88·	24.2·	23.1·	60·	7.4·	20.8·	27.1·	52·	15·
Fe(II)	—	86+	43.7+	63	67.7	0	32.8·	37.7·	61·	22.6
Mo(VI)	—	100	51·	22.4	63.2·	0	9.3·	17.5·	21.9·	10.2·
V(IV)	13.3·	88·	56.9·	50.7	67.7·	38.5	42.5·	50.8·	66·	38.3
Zr(IV)	0	0	0	0	0	0	0	0	0	0
Ti(IV)	16.6	94	0	71·	85.1	37.7	86.5	71	85	81.5
Fe(III)	30	47·	58.4·	24.6	74.8·	56.8·	81.8+	50·	73·	74.6+
Al(III)	24·	88·	55.9	50.7	67.7·	38.5·	42.5·	50.8·	66·	36.3
Mg(II)	3.3	0	5.1	0	32.2	0	16.7·	62	—	35.6

. Diffusion,
+ Tailings.

TABLE 4—PAPER ELECTROPHORETIC MOBILITIES OF CERTAIN METALLIC IONS

Paper—Whatman No. 1. Time—2 hrs.
c=cathodic ; a=anodic. Voltage—200 v.
''=Broad Band.

Metallic Ions	Distance moved in mm by the ion					
	A	B	C	L	N	O
Fe(II)	5 c''	0	7 c''	0	22 c	5 c
Co(II)	7 c''	10 c	32 c''	15 c''	27 c''	34 c''
Ni(II)	7 c''	15 c	40 c''	18 c''	8 c''	31 c''
Cu(II)	9 c''	9.5 c''	44 c''	17 c	10 c'	30 c
Mn(II)	8 c''	0	5 c''	0	14 c	11 c
Zn(II)	18 c''	—	49 c''	27 c''	58 c''	42 c''
Al(III)	11 c''	10 c''	24 c''	22 c	18 c''	26 c''
Mg(II)	12.5 c	6 a''	7 a	20 a	14 c''	5 c
Zr(II)	0	0	7 c	0	0	6 c
V(IV)	10 c''	10 c''	28 c''	32 c''	26 c''	23 c''
U(VI)	0	7 c''	10 c''	0	15 c'	40 c''
W(VI)	8 a	7 a	12 c	7.5 c	8 c	9 c
Mo(VI)	7 a	4 a''	21 a''	5 a	8 c	20 a
Ti(IV)	6 c	7 c	5 c	14 c	8 c	4 c
Cr(III)	0	5 c	13 c	7 c	28 c''	10 c

The abbreviations used for the solvents in the Tables are as follows :

A = Ethanolic Soln. of Van-An.
B = Ethanolic Soln. of Van-Hy.
C = Aq. Soln. of Na.-Sul-Van.
D = A+HCl (1*M*) [10 : 1]
E = A+HCl (1*M*) [20 : 1]
F = A+HCl (1*M*) [25 : 1]
G = A+HCl (1*M*) [5 : 1]

H = A+Acetic acid (1*M*) [10 : 1]
I = A+Acetic acid (1*M*) [5 : 1]
J = B+HCl (1*M*) [10 : 1]
K = B+HCl (1*M*) [5 : 1]
L = B+Acetic acid (1*M*) [10 : 1]
M = B+Acetic acid (1*M*) [5 : 1]
N = A+Py. Buffer [*p*H 6]
O = C+Py. Buffer [*p*H 5.9]

TABLE I—SEPARATION POSSIBILITIES OF METALLIC IONS USING CERTAIN SCHIFF BASES
BINARY SYSTEMS

PC = Paper Chromatography (Radial) ; TLS = Thin Layer (Silica) ;
PE = Paper Electrophoresis ; TLC = Thin Layer (Cellulose).

Ions Separated	Methods and Solvents	Ions Separated	Methods and Solvents
1. Fe(II), Co(II)	PC(C) ; PE (A,B,N,P)	21. Fe(III), V(IV)	PE(A,B,O)
2. Fe(II), Fe(III)	PC(A,B) ; TLC (C,H,J) ; PE (N,O,P)	22. Fe(III), Zr(IV)	PE(A,O) ; TLS(A)
3. Co(II), Ni(II)	PC(A,B,C) ; TLC(D)	23. Fe(II), Ni(II)	TLS(E) ; PE (A,B)
4. Co(II), Cu(II)	PC(C) ; TLS (D,E,H)	24. Fe(II), Zn(II)	PE (A,B)
5. Co(II), Zn(II)	PC(C)	25. Fe(II), Cr(III)	PE (A,B,P)
6. Co(II), Mn(II)	PC(C), PE(B,C,P)	26. Mn(II), Zn(II)	PC(A,B) ; PE(C)
7. Cu(II), Ag(I)	PC(C)	27. Mn(II), Ni(II)	PE(B,C,P)
8. Cu(II), Mn(II)	PE(B,C,P)	28. Mn(II), Cr(III)	PE(B,P)
9. Cu(II), Fe(II)	PE(A,B,P)	29. Mo(VI), W(VI)	PE(C,I)
10. Cu(II), Zn(II)	PE(B)	30. Mo(VI), U(VI)	PE(C)
11. Cu(II), Ni(II)	TLC (A,D,J,M) ; TLS (D,E,H)	31. Mo(VI), V(IV)	PE(C)
12. Cu(II), Fe(III)	TLS (E)	32. Mo(VI), Zr(IV)	PE(C)
13. Cu(II), Cr(III)	PE(A)	33. Mo(VI), Cr(III)	PE(C)
14. Fe(III), Ni(II)	TLS(D)	34. Zr(IV), V(IV)	PE(A)
15. Fe(III), Co(II)	TLS(D,E)	35. U(VI), V(IV)	PE(A,P)
16. Fe(III), Mn(II)	PE(O,P)	36. Al(III), Cr(III)	PC(A)
17. Fe(III), Cr(III)	PE(O)	37. Be(II), Mg(II)	PC(B,C)
18. Fe(III), Mo(VI)	TLS(A), PE(B,C,O)	38. Be(II), Al(III)	PC(C)
19. Fe(III), W(VI)	PE(B,C,O)	39. Mg(II), Al(III)	PC(B) ; TLS(A,B) ; TLC(D,J) ; PE(B,C,O,P)
20. Fe(III), U(VI) *	PF(A,B,O,P)	40. Sr(II), Ba(II)	PC(C)

TABLE II—SEPARATION POSSIBILITIES OF METALLIC IONS USING CERTAIN SCHIFF BASES
TERNARY SYSTEMS

PC=Paper Chromatography (Radial); TLS=Thin Layer (Silica);
PE=Paper Electrophoresis; TLC=Thin Layer (Cellulose).

Ions Separated	Methods and Solvents	Ions Separated	Methods and Solvents
41. Fe(II), Co(II), Cu(II)	TLS(H)	61. Fe(III), Ti(III), Cr(III)	PE(O)
42. Fe(II), Zn(II), Ni(II)	PE(B)	62. Fe(III), Mo(VI), Zr(IV)	TLS(H)
43. Fe(II), Cu(II), Zn(II)	PE(B)	63. Fe(III), V(IV), Zr(IV)	TLS(B); PE(N)
44. Fe(II), Co(II), Zn(II)	PE(B)	64. Fe(III), Ti(IV), Zr(IV)	TLS(B)
45. Fe(II), Ni(II), Cu(II)	TLS(H)	65. Fe(III), Cr(III), Mo(VI)	PC(A,B); PE(B,O)
46. Fe(II), Co(II), Ni(II)	TLC(A,H,J)	66. Fe(III), W(VI), Cr(III)	PE(B)
47. Fe(II), Cr(III), Ni(II)	PE(B)	67. Fe(III), Mo(VI), U(VI)	PE(B)
48. Co(II), Ni(II), Cu(II)	TLS(B,H L)	68. Fe(III), W(VI), U(VI)	PE(B)
49. Cu(II), Zn(II), Mn(II)	PE(B)	69. Fe(III), Mo(VI), W(VI)	PE(C)
50. Mn(II), Zn(II), Co(II)	PE(B)	70. Mo(VI), V(IV), Zr(IV)	TLC(A,B,H)
51. Zn(II), Mn(II), Ni(II)	PE(B)	71. Mo(VI), W(VI), U(IV)	PC(A,B); PE(A P)
52. Zn(II), Cd(II), Hg(II)	PC(A,C)	72. Mo(VI), W(VI), Zr(IV)	PE(A,P)
53. Ag(I), Zn(II), Pb(II)	PC(A,B)	73. Mo(VI), W(VI), Ce(IV)	PC(A,B)
54. Ca(II), Sr(II), Ba(II)	PC(A)	74. Mo(VI), U(VI), Zr(IV)	PE(B)
55. Fe(III), Al(III), Mg(II)	TLS(A,B,E,L); TLC(A); PE(B)	75. Mo(VI), W(VI), Cr(III)	PE(A)
56. Fe(III), Co(II), Ni(II)	TLC(H)	76. U(VI), V(IV), W(VI)	PE(A)
57. Fe(III), Al(III), Cr(III)	TLC(M,C)	77. Mo(VI), Ti(IV), Zr(IV)	TLS(B)
58. Fe(III), Fe(II), Mn(II)	PE(O)	78. Ti(IV), Zr(IV), V(IV)	TLS(A,H,L)
59. Fe(III), Mo(IV), Ti(VI)	PE(B,O)	79. W(VI), U(VI), Zr(IV)	PE(B)
60. Fe(III), Ti(IV), W(VI)	PE(B,O)		

TABLE III—SEPARATION POSSIBILITIES OF METALLIC IONS USING CERTAIN SCHIFF BASES
POLYNARY SYSTEMS

PC=Paper Chromatography (Radial);
PE=Paper Electrophoresis;
TLS=Thin Layer (Silica);
TLC=Thin Layer (Cellulose).

Ion Separated	Method and Solvents
1. Co(II), Ni(II), Cu(II), Mn(II)	PC(B)
2. Fe(II), Ni(II), Cu(II), Zn(II)	PC(A)
3. Cu(II), Zn(II)Pb(II), Zn(II)	PC(A,B)
4. Co(II), Ni(II), Cu(II), Zn(II)	PC(A)
5. Fe(III), Co(II), Ni(II), Cu(II)	TLS(A,L)
6. Fe(II), Ni(II), Cu(II), Mn(II)	PC(B)
7. Fe(III), Mo(VI), Co(II), Ni(II)	TLC(M)
8. Fe(III), Mo(VI), Ti(IV), V(IV)	TLC(H)
9. Fe(III), Zn(VI), V(IV), Ti(IV)	TLC(H)
10. Zr(IV), Cr(III), Mo(VI), Fe(III)	PE(N)
11. Fe(III), Cr(III), Zr(IV), W(VI)	PE(N)
12. Fe(III), Cr(III), Zr(IV), Ti(VI)	PE(N)
13. Mo(VI), V(IV), Zr(IV), Ti(IV)	TLS(D); TLC(J)
14. Mo(VI), U(VI), Ce(IV), V(IV)	PC(A)
15. Fe(III), Mo(VI), V(IV), Zr(IV)	TLC(D)
16. Fe(III), Ti(IV), Mo(VI), Zr(IV)	TLC(J)
17. Mo(VI), Ce(IV), Zr(IV), V(IV)	PC(A)
18. Ag(II), Bi(III), Pb(II), Zn(II), Mn(II)	PC(C)
19. Co(II), Ni(II)/Cu(II), Ag(I), Pt(IV)	PC(A,B)
20. Fe(III), Mo(VI), V(IV), Cr(III), Ti(IV)	TLC(C)
21. Fe(III), Mo(VI), V(IV), Zr(IV), Ti(IV)	TLS(E), TLC(A,C,M)
22. V(IV), Ti(IV), Cu(II), Ni(II), Al(III)	TLS(L); TLC(D)
23. Mo(VI), Al(III), Fe(III) Co(II), Ni(II)	TLS(L), TLC(D)
24. Cu(II), Ag(I), Zn(II), Pb(II), Mn(II), Sn(IV)	PC(A,F)
25. Cu(II), Ag(I), Pt(II), Sn(II), Zn(II), Mn(II), Bi(III), Cd(II)	PC(A)
26. Cu(II) Zn(II), Cd(II) Hg(II), Pb(II), Sn(II), Mn(II), Cd(II)	PC(A)

Results and Discussion

The important results obtained in this study may be summarised as follows:

1. The mobilities of metallic ions on paper were found to increase with the Schiff base present in the solutions (used as the mobile phase) in the order: Van-Hy<Van-An< Van-Sul. TLC-Studies also indicated similar results (i.e. Van-An>Van-Hy).

2. Mobilities of ions on impregnated papers were found faster than on plain papers, while ethyl acetate, acetone, dioxane and chloroform failed to impart mobility to the metallic ions on impregnated papers, ethanol proved quite successful in doing so. However, a comparison of the mobilities of Cu(II), Co(II) and Ni(II) with a standard solvent system, ethyl acetate, acetone and HCl (2*M*) in a (v/v) ratio 9 : 9 : 2, on plain and impregnated papers indicated slower mobilities on impregnated paper.

3. The presence of acid in the solvent was found to accelerate the mobilities of the ions. The acceleration was found greater with a strong acid (HCl) than with a weak acid (acetic acid). Although, effective separations could be affected in the absence of the acid. The spots were diffused in a number of cases. The presence of acid prevents the diffusion, but at the same time the effective separation is lost with HCl, whereas acetic acid helps it, particularly in case of Van-Hy.

4. Paper electrophoretic studies, using same solvents as with paper (or thin layers) did not give fruitful results, because of the overlapping of the bands. However, some better separations could be effected using pyridine buffers with Van-An and Van-Sul and Van-Hy-acetic acid mixture. Similarly, the descending chromatography with the filter paper

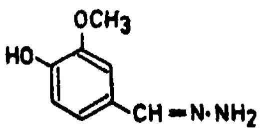
strips, using alcoholic solutions of these Schiff bases were found unsuccessful in effecting differential migration as practically every metal-ion was found to move with the solvent-front.

In the light of the above results, the following mechanism for paper chromatography may be suggested, with the use of solutions of complexing agents in the mobile phase, modifying slightly the working hypothesis of Janardhan and Paul[1]. On plain papers the aquo cation may be considered adsorbed forming ion associated complex with cellulose, as suggested by Janardhan *et al*[1]. On irrigating the paper with a solution of complexing agent (Ligand), the metal ion forms complex with the ligand replacing the bound water molecules partially or wholly. Thus, the metal ion, in the form of metal-ligand complex is only loosely held with the paper and comes in rather desorbed state. The solvent then washes this metal-complex on account of its solvating effect. The release (or presence) of protons during complex formation, however, helps in desorption due to displacement of the metal-ions.

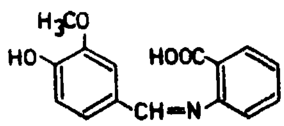
Similarly, on impregnated papers, the presence of complexing agent (Ligand) in the stationary phase—results in the formation of metal-ligand complex during spotting of the aquo cation on paper in place of ion associated metal cellulose complex. Thus, the metal-ion remains rather desorbed in the form of metal-ligand complex and is washed away with the irrigating solvent due to its solvating effect for this complex. The release or presence of protons, plays its catalysing part in the desorption of the metal-ion here also.

Thus, in both the cases of plain and impregnated papers the differential migration of the metallic ions are due to difference in the solubilities of the metal-ligand complex in the solvent. The lack of mobilities of metallic ions on impregnated papers with pure organic solvents dioxane, ethylacetate, acetone and chloroform was associated with the insolubility of the metal-ligand complexes in these solvents. As these complexes are soluble in ethanol, it was found successful in giving mobilities to the metallic ions.

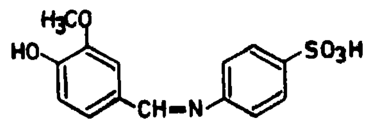
The reverse order of mobility of the Cu(II), Co(II) and Ni(II) on plain and impregnated paper, with the standard solvent system can also be understood in the light of lesser solubilities of these complexes in aqo-HCl resulting in the lesser mobilities on impregnated paper. The other components of the solvent—system, ethyl acetate and acetone have no solvating effect on these complexes. As the release or the presence of protons (acid) helps in desorption of the metal-ion, the observed order of mobilities of the metallic ions with the Schiff-base present in the solution : Van-Hy $<$ Van-An $<$ Van-Sul and the accelerating effects of the presence of acids, strong and weak (HCl and Acetic acid) can be explained in the light of their proton releasing tendencies (acid-strengths). The acid-strengths of Van-Hy, Van-An and Van-Sul, show an increasing trend with the replacement of hydrazine by anthranilic acid in Van-An(II) and by sulphanilic acid in Van-Sul(III)



(I) Van-Hy.



(II) Van-An.



(III) Van-Sul.

The greater mobilities of metallic ions in presence of HCl than acetic acid can similarly be understood. Lesser diffusion in presence of an acid is also associated with the ease of desorption of metal ions, thus giving more compact bands. HCl, being a strong acid, causes a levelling effect to the mobilities of metallic ions. Thus, acetic acid (a weak acid) was found more useful in giving effective separations.

References

1. P. B. JANARDHAN and A. PAUL, *Indian J. Chem*, 1967, 5, 297.
2. C. MICHAELIS, N. S. TARLANO, J. CLUNE and R. S. YOLLES, *Anal. Chem.*, 1962, 34, 1425.
3. C. MICHAELIS, S. EVESLAGE, P. COULTER and J. FORTMAN, *Anal. Chem.*, 1962, 34, 1764.
4. L. RUTTER, *Nature*, 1948, 161, 435.
5. A. I. VOGEL. "*A Text Book of Quantitative Inorganic Analysis*", Longmans Green & Co. Ltd., London, 1962, p. 729.
6. A. I. VOGEL, "*A Text Book of Macro and Semimicro Qualitative Inorganic Analysis.*" Longmans, IV Edition, 1957, pp. 623-31.

J. Indian Chem. Soc.,
Vol. LVII, June 1980, pp. 591-595

Adsorption Behaviour of Some Metal Ions on Cation-Exchange Resin (Dowex 50W-X4) from Ammonium Acetate-Dimethylformamide Media

BINOY K. GHOSH, ASHOK MAHAN, ANIMESH K. GHOSE and ARUN K. DEY*

Chemical Laboratories, University of Allahabad, Allahabad-211 002

Manuscript received 25 June 1979, revised 15 April 1980, accepted 13 May 1980

The cation-exchange (by Dowex 50W-X4; NH_4^+-form) characteristics of 17 metal ions in media consisting of 40% DMF and varying concentrations (0.02-1.00*M*) of NH_4OAc have been reported. To ensure maximum adsorption, the metal concentrations employed were kept ca 16% of the total exchange capacity of the resin. The values of distribution coefficients have been evaluated, and possible separations of metal ions have been predicted. Some of the useful separations have been achieved using column chromatography.

ION-EXCHANGE characteristics of metal ions have largely been studied in ammonium acetate media and several metal ions have successfully been separated. The separations of Ba(II), Pb(II)[1], and of Mg(II), Ca(II), Sr(II) and Ba(II)[2] on R-NH_4 type resin in aqueous NH_4OAc have been investigated. Ward and Choppin[3] determined the separation factors by column elution for Ce, Pm, Eu, Tb, Tm and Y using Dowex 50 and NH_4OAc solutions. A method for the ready separation of silver, lead and mercury(II) from each other has been developed by De and Majumdar[4]. In 1*M* acetate buffer, De and Sen[5] were able to separate calcium and magnesium in dolomite and limestone. Dey and coworkers[6,7] studied the adsorption behaviour of certain cations in HNO_3-NH_4OAc and aqueous NH_4OAc, and reported an interesting procedure of separation of Ce(IV) from Ce(III), La(III) and other metal ions[7].

The use of organic solvents in ion exchange separations of metals has become common place and hardly requires comment[8]. Since dimethylformamide is increasingly coming into use as a solvent, and mixed water-DMF solvents are now better understood, a detailed study of adsorption characteristics of the seventeen cations: Mg(II), Al(III), Ca(II), Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Sr(II), Ag(I), Cd(II), Ba(II), La(III), Hg(II), Pb(II) and Th(IV), have been investigated in 40% v/v DMF-aq NH_4OAc media, using Dowex 50W-X4 (200-400 mesh, NH_4^+-form) to exploit the possibility of better separations of the cations.

Experimental

Ion-Exchange Resin :

Dowex 50W-X4 (200 – 400 mesh) in H^+-form was treated in a column successively with 1*N* HCl and 1*N* NaOH before use. The resin was then converted into NH_4^+-form by treating with 10% NH_4Cl solution in 10% liquor ammonia (Sp. gr. 0.91) and then washing with water till the effluent was free from chloride (negative test with $AgNO_3$). The resin was air-dried by suction on a sintered bed and stored, the capacity and the moisture content were 3.14 meq/g and ca 27.25%, respectively.

Metal Solutions :

Standard aqueous solutions (0.10-0.50*M*) of metal ions were prepared from their nitrates (B.D.H., AnalaR). Hg(II) nitrate was dissolved in aq NH_4OAc. The solutions were standardized as usual.

Ammonium Acetate Solution :

An aqueous solution of 6.0*M* NH_4OAc (E. Merck) was prepared and was standardized by the indirect determination of ammonia.

Buffer Solutions :

Buffer solutions of *p*H = 10 (NH_4Cl/ammonia) and of *p*H = 5 (NaOAc/HCl) were used for EDTA titrations. Other desired *p*H were obtained by maintaining the *p*H of the solution by the addition of suitable quantities of acid or alkali and with the help of a *p*H-meter. *p*H indicator papers (B.D.H.) were also used in some cases during titrations.

Organic Solvent :

Reagent-grade dimethylformamide (B.D.H.) was used.

pH Measurements and Equilibration of the System :

A Philips precision *p*H-meter PR 9405M was employed for the *p*H measurements. The solutions

* To whom all correspondence should be addressed.

were mechanically shaken using a reciprocating shaker (Sambros & Co., SR. No. SE 037) in glass-stoppered pyrex flasks (100 ml) in batch experiments.

Distribution Studies

For the determination of distribution coefficients (D) by the batch equilibration method, 1.000 gram of the air-dried resin (NH_4^+-form) was added to the mixture solutions containing the metal ion, DMF and NH_4OAc (total volume 25 ml), and shaken for 1 hr (it was previously ascertained that this time was adequate to attain equilibrium). The resin was filtered and the metal ion determined in an aliquot of the filtrate titrimetrically against EDTA, and the D values were obtained

$$D = \frac{\text{meq. metal ion per gram resin}}{\text{meq. metal ion per ml solution}} \quad \ldots \quad (1)$$

The metal concentrations employed were ca 16% of the total exchange capacity of the resin, to ensure maximum intake by the resin. Aqueous NH_4OAc used were 0.02, 0.06, 0.10, 0.25, 0.50 and 1.00M and DMF was 40%. Studies were made at a room temperature of $30\pm2°$. The relative experimental errors in the determination of the D values were $\pm$ 10% and $\pm$ 20% for low and high D values, respectively.

Column Chromatography :

Before the chromatographic separations, the resin bed was prepared by making a slurry of the resin (5.0 g) in water and transferred to the graduated column. The length of the resin bed was ca 6 cm. The resin bed thus prepared was pretreated with 0.10M, 0.25M or 0.50M NH_4OAc as the case may be.

The feed (25 ml) was prepared by mixing standard solutions of the metal ions and aq. NH_4OAc (of appropriate concentration) and 40% DMF. It was then passed through the resin bed and the rate of flow was adjusted to 1.0 ± 0.3 ml per minute. The metal ions were determined in 5 ml effluent fractions.

Results and Discussion

The distribution coefficient (D) of the cations are reported in Table 1. In all the cases the sorption of metal ions decreases with increasing the concentrations of NH_4OAc (DMF being constant). Generally, the metal ion forms a complex with the acetate ion and the sorption depends upon the nature of complex formed. If the charge on the complex is positive, zero or negative, the sorption will be less. The concentration 40% of DMF has been found to be best for separations, by trial experiments.

TABLE 1—VALUES OF DISTRIBUTION COEFFICIENTS (D) IN NH_4OAc-40% DMF ($30\pm2°$)

Cation	Distribution Coefficient (a)	(b)	(c)	(d)	(e)	(f)
Mg(II)	856	195	110	40.3	14.8	1.1
Al(III)	$>10^4$	$>10^4$	$>10^4$	2730	38.3	8
Ca(II)	581	293	184	36.2	15.4	4.1
Cr(III)	1810	272	97.2	19.6	11.8	7.1
Mn(II)	424	236	111	24.5	7	0.4
Co(II)	686	255	121	31	7.6	1.2
Ni(II)	851	224	125	30.7	7.6	1.5
Cu(II)	428	90.4	38.7	7.2	1.6	0.0
Zn(II)	422	142	60	9.7	0.2	0.0
Sr(II)	1070	578	284	93.2	81	9.5
Ag(I)	95.7	52.4	86.5	(*)	(*)	(*)
Cd(II)	429	107	46.7	7.0	0.3	0.0
Ba(II)	8070	784	438	190	57.8	20.7
La(III)	984	984	342	44.2	5.6	0.6
Hg(II)	(*)	(*)	(*)	140	45.8	9.7
Pb(II)	332	67	27.6	4.3	0.5	0.0
Th(IV)	$>10^4$	$>10^4$	6130	77.5	9.8	0.5

Overall concentrations of ammonium acetate (M) : (a) = 0.02 ; (b) = 0.06 ; (c) = 0.10 ; (d) = 0.25 ; (e) = 0.50 ; (f) = 1.00 ; (*) = precipitation.

As the concentration of NH_4OAc is increased, acetate ion replaces the coordinating water molecules resulting in the formation of complex species of a small positive charge, and consequently D is lowered. A further increase in the concentration of NH_4OAc leads to the formation of a neutral species and this also results in a decrease of D. When the concentration of NH_4OAc is higher, and a neutral metal acetate is likely to be present in solution, the predominant species in the resin phase would be $M^{II}(OAc)^+$ or $M^{III}(OAc)^{2+}$, as inferred by earlier workers[8,9].

It is of interest to refer to the work of Strelow and coworkers[8], in which a detailed cation exchange study of a large number of metal ions has been reported from ethanol-HCl mixtures. The table of distribution coefficients clearly indicates that the role of ethanol is mainly to assist the formation of chlorocomplexes by influencing the dielectric constant of the media. In a likewise manner, in the work reported here, the role of DMF is also similar, and DMF does not display a complexing ability in the systems.

Ag(I) has slightly lower D values, whereas Al(III) and Th(IV) have slightly higher D values at lower concentration (0.02 M) of NH_4OAc, which is due to the higher affinity of ammonium ions towards the resin as compared to Ag^+, and the reverse is true for Al(III) and Th(IV). Also, the sorption of Al(III) and Th(IV) is high in 0.1M NH_4OAc as compared to the other metal ions, which is due to the higher charge on these cations. The D values of Cu(II), Zn(II), Cd(II) and Pb(II) are zero in 1.0M NH_4OAc, whereas Ba(II) has a slightly higher D value ; hence Ba(II) can be separated from Cu(II), Zn(II), Cd(II) and Pb(II) in this concentration

range of NH_4OAc. The percentage loadings* of the metal ions under experiment are plotted against concentrations of ammonium acetate. In order to avoid overlapping of the plots for other cations, they have been divided into two groups,

(1) Mg(II), Ca(II), Ni(II), Sr(II), Ag(I), Cd(II), Ba(II), La(III), Pb(II) and Th(IV), and

(2) Al(III), Cr(III), Mn(II), Co(II), Cu(II), Zn(II) and Hg(II),

and shown separately in Figs. 1 and 2, respectively, which illustrate the separation possibilities.

Table 2 represents the variation of sorption of cations at the different concentrations of NH_4OAc

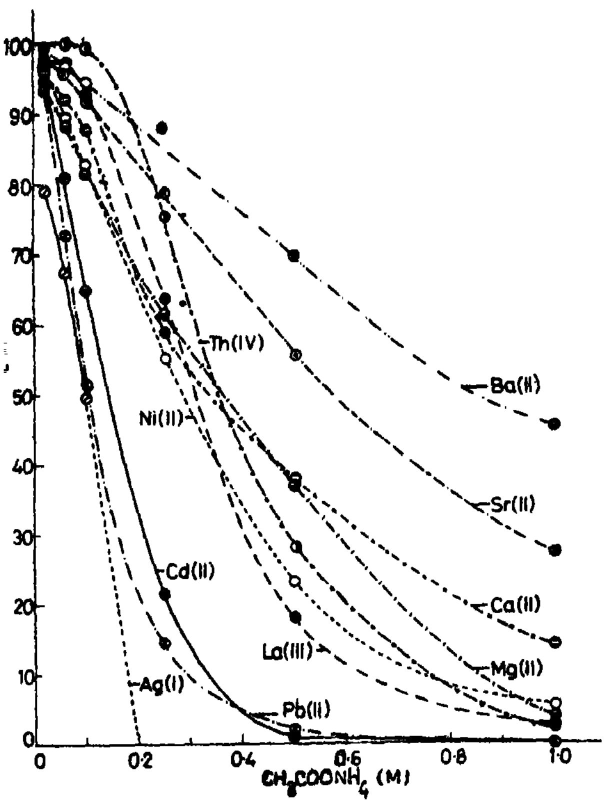


Fig. 1. Plot of Loading percentage *vs* concentration of ammonium acetate.
Mg(II), Ca(II), Ni(II), Sr(II), Ag(I), Cd(II), Ba(II), La(III), Pb(II) and Th(IV).

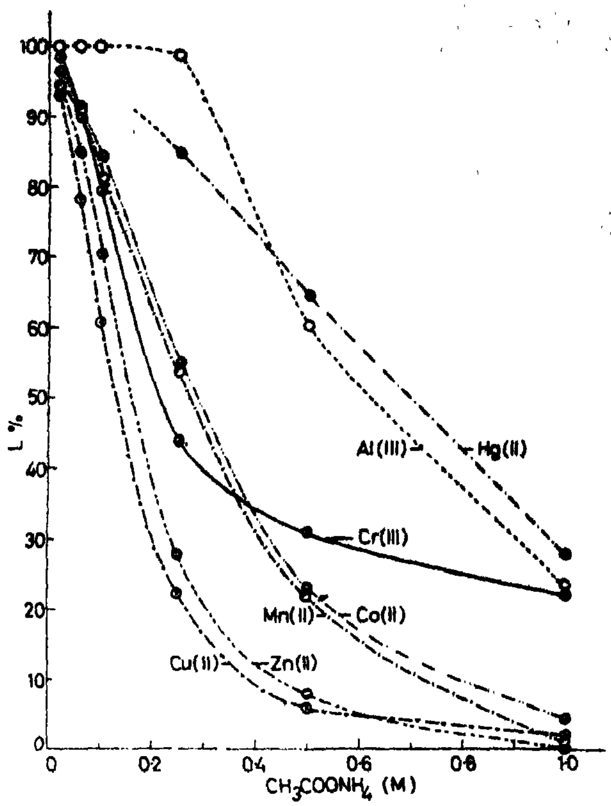


Fig. 2. Plot of Loading percentage *vs* concentration of ammonium acetate.
Al(III), Cr(III), Mn(II), Co(II), Cu(II), Zn(II) and Hg(II).

in 40% DMF. Few important chromatographic separations, i.e.

(i) Th(IV) and Cu(II),
(ii) Hg(II) and Pb(II)/Zn(II)/Cd(II),
(iii) Al(III) and Cu(II)/Zn(II)/Pb(II)/Cd(II)/Mn(II)/Cr(III)

were achieved at 0.10*M*, 0.25*M* and 0.50*M* NH_4OAc and few of them are shown in Figs. 3, 4 and 5, respectively. The elution characteristics[10] are shown in Table 3, while Table 4 shows the quantitative values. Some of the binary separations are important, as may be seen from the Table.

TABLE 2—VARIATION OF SORPTION OF CATIONS WITH THE CONCENTRATION OF AMMONIUM ACETATE (OVERALL DMF 40%)

$[NH_4OAc]$	Sorption order
1. 0.02	$Al \approx Th > Ba > Cr > Sr > La > Ni > Co > Ca > Cd \geqslant Cu \geqslant Mn \geqslant Zn > Mg > Pb > Ag$
2. 0.06	$Al \approx Th > La > Ba > Sr > Ca > Cr > Co > Mn > Ni > Mg > Zn > Cd > Cu > Pb > Ag$
3. 0.10	$Al > Th > Ba > La > Sr > Ca > Ni \geqslant Co > Mn \geqslant Mg > Cr > Zn > Cd > Cu \geqslant Ag > Pb$
4. 0.25	$Al > Ba > Hg > Sr > Th > La \geqslant Mg > Ca > Co \approx Ni > Mn > Cr > Zn \geqslant Cu \geqslant Cd > Pb$
5. 0.50	$Ba > Hg > Al > Sr > Ca > Mg > Cr > Th > Co \approx Ni \approx Mn \geqslant La > Cr > Pb > Cd \approx Zn$
6. 1.00	$Ba > Hg \approx Sr \geqslant Al \geqslant Cr > Ca > Ni \geqslant Co \geqslant Mg > La > Th \geqslant Mn > Zn \approx Cu \approx Cd \approx Pb$

$$^{*}L(\%) = \frac{\text{meq. of metal/g of resin}}{\text{meq. of metal initially taken}} \times 100,$$

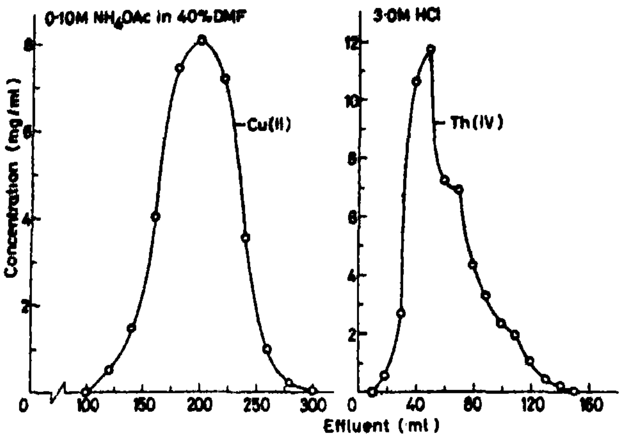


Fig. 3. Elution curves of Cu(II) and Th(IV) on Dowex 50W-X4 Resin (200–400 mesh, NH_4^+-form) column.

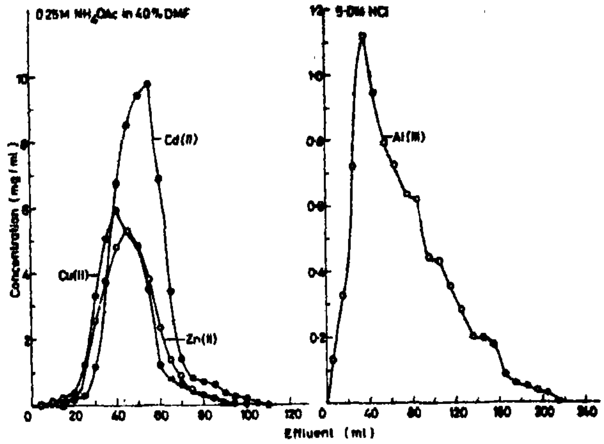


Fig. 5. Elution curves of Al(III)–Cu(II)/Zn(II)/Cd(II) on Dowex 50w-X4 resin (200-400 mesh, NH_4^+-form) column.

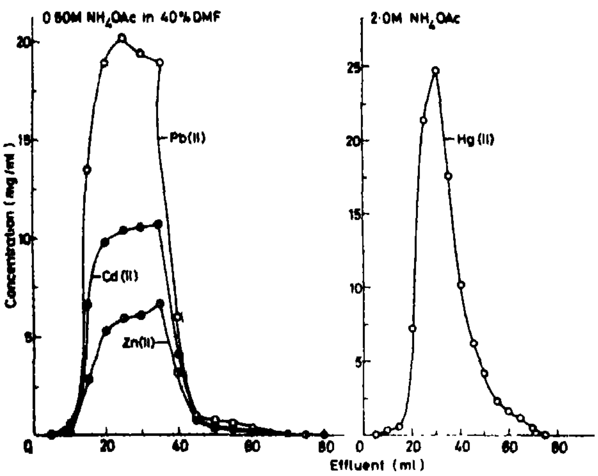


Fig. 4. Elution curves of Hg(II)-Zn(II)/Cd(II)/Pb II) on Dowex 50W-X4 resin (200-400 mesh NH_4^+-form) column.

TABLE 3—ELUTION CHARACTERISTICS[10] OF METAL IONS

Metal Ions	BTV (ml)	VEP (ml)	TEV (ml)	Eluting agent NH_4OA in 40% DMF [M]
Cu(II)	100	200	300	0.10
Cu(II)	20	40	95	0.25
Zn(II)	10	45	105	0.25
Pb(II)	10	45	90	0.25
Cd(II)	5	55	110	0.25
Mn(II)	35	105	345	0.25
Cr(III)	15	70	230	0.25
Pb(II)	10	25	70	0.50
Zn(II)	10	35	80	0.50
Cd(II)	10	35	70	0.50

BTV = breakthrough volume, VEP = volume elution peak, TEV = terminal elution volume.

TABLE 4—QUANTITATIVE SEPARATION OF SYNTHETIC MIXTURES. (FIRST ION MENTIONED IN THE MIXTURE IS ELUTED, WHILE THE SECOND ION IS THAT WHICH IS RETAINED)

Mixture	Eluting agent	Metal ion eluted		Eluting agent	Metal ion retained	
		Taken (mg)	Found (mg)		Taken (mg)	Found (mg)
Cu(II)-Th(IV)	(d)	32.89	33.23±0.46	(a)	52.79	53.25±0.29
Cu(II)-Al(III)	(e)	32.89	32.85±0.12	(b)	8.39	8.49±0.12
Zn(II)-Al(III)	(e)	32.46	33.04±0.55	(b)	8.39	8.36±0.10
Pb(II)-Al(III)	(e)	105.05	104.86±0.16	(b)	8.39	8.39±0.08
Cd(II)-Al(III)	(e)	54.07	54.92±0.64	(b)	8.39	8.40±0.14
Mn(II)-Al(III)	(e)	27.88	27.94±0.10	(b)	8.39	8.38±0.12
Cr(III)-Al(III)	(e)	16.12	15.82±0.24	(b)	8.39	8.46±0.12
Pb(II)-Hg(II)	(f)	101.32	101.28±0.18	(c)	96.27	97.56±0.86
Zn(II)-Hg(II)	(f)	32.43	32.72±0.28	(c)	96.27	96.88±0.24
Cd(II)-Hg(II)	(f)	54.07	54.47±0.10	(c)	96.27	97.05±0.55

(a) 8*M* HCl, (b) 5*M* HCl, (c) 2*M* aq NH_4OAc, (d) 0.1*M* NH_4OAc in 40% DMF, (e) 0.25*M* NH_4OAc in 40% DMF. (f) 0.5*M* NH_4OAc in 40% DMF.

References

1. E. MINAMI and T. ISHIMORI, *J. Chem. Soc.*, Japan, 1953, **74**, 378.
2. M. HONDA, *Japan Analyst*, 1954, 3, 132.
3. B. H. WARD and G. R. CHOPPIN, *J. Inorg. Nuclear Chem.*, 1965, **27**, 459.
4. A. K. DE and S. K. MAJUMDAR, *Talanta*, 1963, **10**, 201.
5. A. K. DE and A. K. SEN, *Talanta*, 1966, **13**, 1313.
6. A. MAHAN, A. K. GHOSE and A. K. DEY, *Sep. Science*, 1971, **6**, 781.
7. L. C. T. EUSEBIUS, A. MAHAN, A. K. GHOSE and A. K. DEY, *Indian J. Chem.*, 1977, **15A**, 438.
8. H. F. WALTON, *Anal. Chem.*, 1970, **42**, 92R; F. W. E. STRELOW, C. R. VAN ZYL and C. J. C. BOTHONA, *Anal. Chim. Acta*, 1969, **45**, 81.
9. E. BRUCHER and P. SZARKAS, *J. Inorg. Nuclear Chem.*, 1966, **28**, 2361.
10. G. E. JANAUER, J. KORKISCH and S. A. HUBBARD, *Talanta*, 1971, **18**, 767.

J. Indian Chem. Soc.,
Vol. LVII, June 1980, pp. 596-600

Ternary Complexes : Equilibrium Study of the Mixed Complexes of Uranyl Ion with Dipicolinic Acid as a Primary Ligand and Some Dicarboxylic Acids as Secondary Ligands*

D. N. SHELKE**

Department of Chemistry, Marathwada University, Aurangabad-431 004, India

and

D. V. JAHAGIRDAR

Department of Chemistry, Georgia State University, University of Plaza, Atlanta, Georgia-30303, U.S.A

Manuscript received 20 February 1979, revised 9 February 1980, accepted 19 May 1980

A pH titration method has been used to determine the equilibrium constants for the mixed-ligand systems of uranyl ion with dipicolinic acid as primary ligand and malonic, succinic, itaconic, glutaric, adipic, thiomalic, thiodiglycolic and thiodipropionic acids as secondary ligands at 30° and ionic strength $\mu=0.1M$ ($NaClO_4$). Dipicolinic, malonic and glutaric acids form 1 : 1 and 1 : 2 chelates with uranyl ion while remaining acids form only 1 : 1 chelate in the pH range 2.5-5.0. It is observed that the coordination of UO_2^{2+} with thiodicarboxylic takes place through oxygens of carboxylate groups, whereas dipicolinic acid bonds through N–O donor atoms filling the equitorial position of coordination sphere of the metal ion. The preferential formation of ternary complexes over binary ones have been discussed on the basis of ring size of chelating acid, basicity of the secondary ligands and the distribution of simple and mixed species present as a function of pH.

DURING recent years intensive investigations have been carried out on the mixed-ligand systems of metal ion with biologically important ligands[1-4]. Recently Gergely and Nagypal[5] have studied the mixed-ligand complexes of Cu^{2+}-dipeptide-amino acids. Although a considerable number of complexes of UO_2^{2+}-carboxylate with amino acids[6,7], dicarboxylic[8,9] and thiodicarboxylic[10] acids have been investigated previously, no work has been published on UO_2^{2+} pyridine dicarboxylic-thiodicarboxylic acids. However, it is surprising that a single system of UO_2^{2+}-dipicolinic-thiodicarboxylic acid has not been studied todate. In view of the above, the present work is carried out to examine the complexing ability of thiodicarboxylic acids with UO_2^{2+}-dipicolinic binary complexes and to discuss the preferential formation of ternary complexes over binary ones.

Experimental

The chemicals used were Fluka, purum products. The concentrations of metal ion was estimated by using the standard procedure[11]. Details of other reagents are given in an earlier paper[12]. All pH measurements were made with a Elico digital pH meter model L 1-120 (No. 1275) with a glass and calomel electrode assembly at 30±0.1° and an ionic strength 0.1 *M* ($NaClO_4$). The accuracy of pH meter was ±0.01 pH units. The pH meter was standardized before each titration by potassium hydrogen phthalate buffer with pH value of 4.01 at 30°. A value of 0.83 for the activity coefficient of 0.1 *M* (H^+) was used in conversion of pH values to hydrogen ion concentrations[13]. A steady steam of nitrogen gas, freed from carbon dioxide, was passed through the solution during titration.

Results and Discussion

Acid dissociation constants of the ligands and stability constants of simple uranyl complexes were evaluated by the method of Irving and Rossotti[14]. The method of calculation of equilibrium constant of ternary complexes, used in the present work has been developed by Ramamoorthy and Manning[15]. The equilibrium constant K_{MXY} for the reaction :

$$MY+H_2X \rightleftharpoons MXY+2H \quad \dots (1)$$

$$K_{MXY}=\frac{[MXY][H]^2}{[MY][H_2X]} \quad \dots (2)$$

is calculated. According to this method the concentrations of total metal ion (C_M), ligand (C_X), ligand (C_Y) and hydrogen ion (C_H) are distributed as follows :

$$C_M=[M]+[MX]+[MX_2]+[MY]+[MY_2]+[MXY] \quad \dots (3)$$

* Paper presented at Chemists Convention, Waltair, 1978.
** To whom all correspondence should be addressed.

$$C_X=[X]+[HX]+[H_2X]+[MX]+2[MX_2]+[MXY] \quad \ldots (4)$$

$$C_Y=[Y]+[HY]+[H_2Y]+[MY]+2[MY_2]+[MXY] \quad \ldots (5)$$

and

$$C_H=[H]+[HX]+2[H_2X]+[HY]+2[H_2Y] \quad \ldots (6)$$

The total available hydrogen ions at any point in the titration curve is given by the expression :

$$C_H=2C_X+2C_Y+P-C_B \quad \ldots (7)$$

where P, is the total concentration of perchloric acid, C_H=total titrable hydrogen ion and C_B= NaOH added. This method is for the calculations of equilibrium constants for the mixed ligand complexes involving two dibasic ligand acids which form 1 : 1 and 1 : 2 binary complexes with the metal ion individually.

From the above equation and dissociation constants of ligands, K_{1X}, K_{2X}, K_{1Y} and K_{2Y}, we get

$$[H_2X]=a-b[H_2Y] \quad \ldots (8)$$

where

$$a=\frac{2C_X+2C_Y+P-C_B-[H]}{2+K_{1X}/[H]} \quad \ldots (8a)$$

and

$$b=\frac{2+K_{1Y}/[H]}{2+K_{1X}/[H]} \quad \ldots (8b)$$

$[H_2Y]$ is calculated from a third degree equation

$$A_1[H_2Y]^3+A_2[H_2Y]^2+A_3[H_2Y]+A_4=0 \quad \ldots (9)$$

where

$$A_1=-b^3d_xf_x+bd_xf_y-d_yf_y+b^2d_yf_x,$$

$$A_2=b^2d_xe_x+3ab^2d_xf_x-ad_xf_y-b^2c'_xf_x+c'_xf_y-d_ye_y-2abd_yf_x+c'_yf_y-b^2c'_yf_x,$$

$$A_3=-bd_x-2abd_xe_x-3a^2bd_xf_x+bc'_xe_x+2abc'_xf_x-d_y+a^2d_yf_x+c'_ye_y+2abc'_yf_x,$$

and

$$A_4=ad_x+a^2d_xe_x+a^3d_xf_x-c'_x-ac'_xe_x-a^2c'_xf_x+c'_y-a^2c'_yf_x,$$

where in turn,

$$C'_X=C_X-C_M \qquad C'_Y=C_Y-C_M$$

$$d_x=1+K_{1X}/[H]+K_{1X}K_{2X}/[H]^2,$$

$$d_y=1+K_{1Y}/[H]+K_{1Y}K_{2Y}/[H]^2,$$

$$e_x=K_{MX_1}K_{1X}K_{2X}/[H]^2,$$

$$e_y=K_{MY_1}K_{1Y}K_{2Y}/[H]^2,$$

$$f_x=K_{MX_1}K_{MX_2}(K_{1X}K_{2X})^2/[H]^4, \text{ and}$$

$$f_y=K_{MY_1}K_{MY_2}(K_{1Y}K_{2Y})^2/[H]^4,$$

where, K_{1X}, K_{2X}, K_{1Y} and K_{2Y} are first and second dissociation constants of ligand (X) and (Y) respectively and K_{MX_1}, K_{MX_2}, K_{MY_1} and K_{MY_2} are the stability constants of simple complexes from equation (9) was obtained by equating equations (10) and (11) :

$$M^{2+}=\frac{[H_2X]\{1+K_{1X}/[H]+K_{1X}K_{2X}/[H]^2\}+C_M-C_X}{1+[H_2Y]K_{MY_1}K_{1Y}K_{2Y}/[H]^2+[H_2Y]^2K_{MY_1}K_{MY_2}(K_{1Y}K_{2Y})^2/[H]^4}-[H_2X]^2K_{MY_1}.K_{MX_2}(K_{1X}K_{2X})^2/[H]^4 \quad \ldots (10)$$

$$M^{2+}=\frac{[H_2Y]\{1+K_{1Y}/[H]+K_{1Y}K_{2Y}/[H]^2\}+C_M-C_Y}{1+[H_2X]K_{MX_1}K_{1X}K_{2X}/[H]^2+[H_2X]^2K_{MX_1}K_{MX_2}(K_{1X}K_{2X})^2/[H]^4}-[H_2Y]^2K_{MY_1}K_{MY_2}(K_{1Y}K_{2Y})^2/[H]^4 \quad \ldots (11)$$

resulting from the equations (6)-(13) and those for the concentrations of simple complexes MX_1, MX_2, MY_1 and MY_2.

The IBM 370/155-II electronic computer was used to calculate :

(i) $[H_2Y]$ from equation (9)

(ii) $[H_2X]$ from equation (8)

(iii) $[M^{2+}]$ from M^{2+}

$$=\frac{d_x[H_2X]+d_y[H_2Y]-C'_X-C'_Y}{2+e_x[H_2X]+e_y[H_2Y]} \quad \ldots (12)$$

(iv) $[MX]=K_{MX_1}K_{1X}K_{2X}[M^{2+}][H_2X]/[H]^2 \quad \ldots (13)$

(v) $[MX_2]=K_{MX_1}K_{MX_2}[M^{2+}](K_{1X}K_{2X}[H_2X])^2/[H]^4 \quad \ldots (14)$

(vi) $[MY]=K_{MY_1}K_{1Y}K_{2Y}[M^{2+}][H_2Y]/[H]^2 \quad \ldots (15)$

(vii) $[MY_2]=K_{MY_1}K_{MY_2}[M^{2+}](K_{1Y}K_{2Y}[H_2Y])^2/[H]^4 \quad \ldots (16)$

(viii) $[MXY]=C_M-[M^{2+}]-[MX]-[MX_2]-[MY]-[MY_2] \quad \ldots (17)$

and

(ix) $K_{MXY}=[MXY][H]^2/[MY][H^2X]$

The equilibrium constants β_{XY}, K_{DXY}, K_{2XY} and K_{2YX} were obtained from K_{MXY} using equations

(18)-(21), namely,

$$\beta_{XY} = K(M+X+Y \rightleftharpoons MXY) = K_{MXY}K_{MY_1}/K_{1X}K_{2X} \quad \dots (18)$$

$$K_{DXY} = K(MX_2+MY_2 \rightleftharpoons 2MXY) = (\beta_{XY})^2/(K_{MX_1}K_{MX_2}K_{MY_1}K_{MY_2}) \quad \dots (19)$$

$$K_{2XY} = K(MX+Y \rightleftharpoons MXY) = K_{MXY}K_{MY_1}/K_{1X}K_{2X}K_{MX_1} = \beta_{XY}/K_{MX_1} \quad \dots (20)$$

and

$$K_{2YX} = K(MY+X \rightleftharpoons MXY) = K_{MXY}/K_{1X}K_{2X} = \beta_{XY}/K_{MY_1} \quad \dots (21)$$

The concentration of the species H_2Y, H_2X, M^{2+} MX, MY, MY_2^{2-} and MXY^{2-} were calculated by using IBM 370/155 II-electronic computer at Indian Institute of Technology, Madras. Calculated concentration of the species present and their corresponding equilibrium constants for the systems UO_2^{2+}-dipicolinic-thiodicarboxylic acids are given in Fig. 1. and Tables 1 and 2. The average equilibrium constants for other systems are given in Table 3.

The stability of ternary complexes is given by $\Delta \log K$ values,

$$\Delta \log K = \log K^{MX}_{MXY} - \log K^{M}_{MY} = \log K^{MY}_{MYX} - \log K^{M}_{MX},$$

one would expect the negative $\Delta \log K$ for the formation of ternary complexes[16,4]. It is also reported in the literature that positive $\Delta \log K$ values for mixed ligand complexes indicating thereby the equilibrium $MX+MY \rightleftharpoons MXY^{2-}+M^{2+}$ is more on right side[4]. Another method of characterization of ternary complexes is by the use of constants

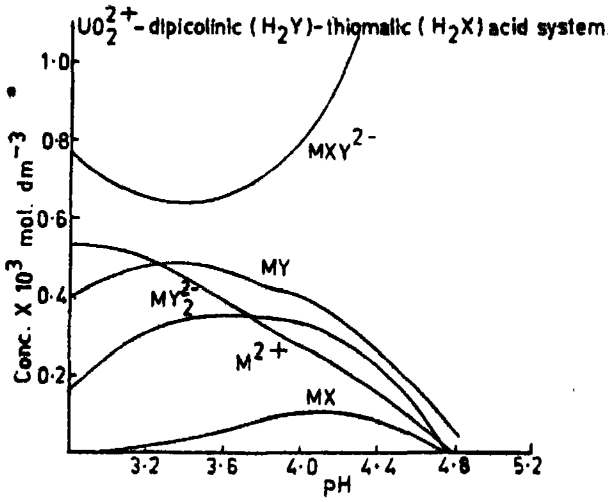


Fig. 1. Distribution of various species present in the ternary uranyl ion-dipicolinic (H_2Y)-thiomalic (H_2X) acid system as a function of pH. M^{2+} = uranyl ion free, MX = uranyl ion-thiomalic acid, MY = uranyl ion-dipicolinic acid, MY_2^{2-} = uranyl ion (dipicolinic acid)$_2$ and MXY^{2-} = uranyl ion-thiomalic-dipicolinic acid. μ = 0.1M ($NaClO_4$). Temp. 30±0.1°, $C_M = C_X = C_Y = 2.0 \times 10^{-3} M$.

Table 1—UO_2^{2+}-Dipicolinic (H_2Y)-Thiodiglycolic (H_2X) Acid System
Calculated Concentrations of M^{2+}, H_2Y, H_2X and Simple and Mixed Species

$C_M = C_X = C_Y$ $\qquad$ μ = 0.1M($NaClO_4$) $\qquad$ Temp. 30±0.1°C

pH	$[H^+] \times 10^4$	$C_B \times 10^3$	$[H_2X] \times 10^4$	$[H_2Y] \times 10^6$	$[M^{2+}] \times 10^4$	$[MY] \times 10^4$	$[MY_2^{2-}] \times 10^4$	$[MX] \times 10^4$	$[MXY^{2-}] \times 10^4$
3.80	1.906	13.120	1.725	1.667	3.084	4.469	4.088	1.771	5.935
3.85	1.699	13.276	1.656	1.427	2.755	4.306	4.247	1.622	6.418
3.90	1.514	13.347	1.429	1.089	2.709	4.068	3.857	1.756	6.944
3.95	1.349	13.422	1.228	0.884	2.598	3.985	3.856	1.830	7.063
4.00	1.203	13.498	1.047	0.717	2.483	3.889	3.845	1.884	7.229
4.05	1.072	13.573	0.884	0.579	2.366	3.772	3.795	1.915	7.477
4.10	0.955	13.648	0.789	0.468	2.246	3.640	3.722	1.917	7.796
4.15	0.851	13.724	0.611	0.376	2.124	3.485	3.609	1.980	8.211
4.20	0.759	13.799	0.498	0.315	1.997	3.307	3.455	1.829	8.729

Table 2—Equilibrium Constants of UO_2^{2+}-Dipicolinic (H_2Y)-Thiodiglycolic (H_2X) Acid System

$C_M = C_X = C_Y$ $\qquad$ μ = 0.1M($NaClO_4$) $\qquad$ Temp. 30±0.1°C

$[H^+] \times 10^4$	K_{MXY}	β_{XY}	K_{DXY}	K^{MX}_{MXY}	K^{MY}_{MYX}
1.906	−1.136	9.234	0.564	5.804	3.794
1.699	−1.094	9.272	0.602	5.842	3.833
1.514	−1.079	9.290	0.620	5.860	3.850
1.349	−1.099	9.271	0.601	5.841	3.831
1.202	−1.111	9.261	0.589	5.829	3.819
1.072	−1.111	9.259	0.589	5.829	3.819
0.955	−1.100	9.269	0.599	5.839	3.829
0.851	−1.077	9.293	0.623	5.863	3.853
0.759	−1.040	9.300	0.660	5.900	3.890
Average	−1.094	9.275±0.03	0.605±0.03	5.845±0.03	3.836±0.03

TABLE 3—LOGARITHMS OF EQUILIBRIUM CONSTANTS OF TERNARY COMPLEXES OF UO_2^{2+}-DIPICOLINIC* (H_2Y)-SECONDARY (H_2X) LIGAND ACIDS

$\mu = 0.1M(NaClO_4)$ Temp. 30±0.1°C

Systems/acid	β_{XY}	K_{DXY}	K^{MX}_{MXY}	K^{MY}_{MYX}	K^{M}_{MX}	$K^{MX}_{MX_2}$	Δlog K
Dipicolinic-malonic	11.15±0.02	2.67^c	5.59	5.71	5.56	3.80	+0.15
Dipicolinic-succinic	9.61±0.03	−0.12^b	5.12	4.16	4.48	—	−0.31
Dipicolinic-itaconic	9.94±0.02	−0.16^b	5.08	4.50	4.86	—	−0.36
Dipicolinic-glutaric	11.07±0.01	5.07^c	7.37	5.68	3.70	2.69	+1.98
Dipicolinic-adipic	9.20±0.03	−0.12^b	5.12	3.76	4.08	—	−0.32
Dipicolinic-thiomalic	9.90±0.02	0.96^b	6.20	4.46	3.70	—	+0.76
Dipicolinic-thiodiglycolic	9.27±0.03	0.60^b	5.84	3.83	3.43	—	+0.40
Dipicolinic-thiodipropionic	9.72±0.01	0.44^b	5.68	4.28	4.04	—	+0.24

* $K^{M}_{MY} = 5.44$; $K^{MY}_{MY_2} = 5.24$.
c = $MX_2^{2-} + MY_2^{2-} \rightleftharpoons 2MXY^{2-}$.
b = $MX_2^{2-} + MY \rightleftharpoons MXY^{2-} + MX$, or $MX + MY_2^{2-} \rightleftharpoons MXY^{2-} + MY$.

$MX_2^{2-} + MY_2^{2-} \rightleftharpoons 2MXY^{2-}$. The value of K_{DXY} expected on statistical basis[17] is 0.6 log units.

In the present investigation dipicolinic acid forms 1 : 1 and 1 : 2 chelates while thiomalic, thiodiglycolic, thiodipropionic acids form only 1 : 1 complexes with uranyl ion in the *p*H range 2.5 to 5.0. Dipicolinic acid can be considered as primary ligand and thiomalic, thiodiglycolic, thiodipropionic which can respectively form seven, eight and ten membered rings, as the secondary ligands. The coordination of UO_2^{2+} with dipicolinic acid can take place through oxygen of carboxylate group and nitrogen of pyridine ring, filling the equatorial positions of the coordination sphere and acid must be tridentate, in agreement with the earlier findings of Edward *et al*[18] and Rayford[19]. In our earlier studies of mixed-ligand complexes, the tridentate nature of dipicolinic acid with transition metal ions, particularly copper ion, has been explained on the basis of structural rearrangement in the mixed-complex[20]. In dipicolinic acid, the chelate ring size is smaller than in quinolinic acid. The difference in log K_1 and log K_2 indicates the formation of 1 : 1 and 1 : 2 chelate formation as almost simultaneous. The chelate ring in the case of UO_2^{2+}-thiomalic acid is found to be stabilized by the neutral sulphur atom while these UO_2^{2+}-thiodiglycolic and UO_2^{2+}-thiodipropionic acid binary complex stabilities are in the expected order of magnitude as indicated by *p*K values.

The formation of MXY^{2-} for UO_2^{2+}-dipicolinic-thiodicarboxylic acid system is considerable around *p*H 2.6. The concentrations of MX and MY_2^{2-} are maximum at around *p*H 3.2 and 3.8 respectively. In all systems, MXY^{2-} curves show an initial fall, followed by a flat minima and then continuously increases with an increase in *p*H. The formation of MX starts from *p*H 3.0, increases up to *p*H 4.1 and then slowly decreases. As a consequence of this, there is an increase in the concentration of MXY^{2-} above *p*H 3.7, though it is almost constant in the *p*H range 3.1-3.6. The formation of simple and mixed species could be represented by the reactions :

K^{M}_{MX} for $M^{2+} + HX^- \rightleftharpoons MX + H^+$ ... (1a)

$K^{MX}_{MX_2}$ for $MX + HX^- \rightleftharpoons MX_2^{2-} + H^+$ ... (1b)

K^{M}_{MY} for $M^{2+} + HY^- \rightleftharpoons MY + H^+$ ... (2a)

$K^{MY}_{MY_2}$ for $MY + HY^- \rightleftharpoons MY_2^{2-} + H^+$ ... (2b)

βXY for $M^{2+} + HY^- + H_2X \rightleftharpoons MHXY^- + 2H^+$ ... (3a)

K^{MY}_{MYX} for $MY + HX^- \rightleftharpoons MXY^{2-} + H^+$ ... (4b)

K^{MY}_{MYX} for $MX + HY^- \rightleftharpoons MXY^{2-} + H^+$ ... (4a)

A perusal of all these graphs reveal a distinct difference in the MXY^{2-} curve of the UO_2^{2+}-dipicolinic-thiodipropionic with the MXY^{2-} curves of the remaining two systems. The reactions (2a and 2b) are favourable for formation of simple species while (3a) is favourable for MXY^{2-} up to *p*H 3.1. The formation of MXY^{2-} is also possible by the reactions :

$$MX + MY \rightleftharpoons MXY^{2-} + M^{2+}$$

and

$$MX + MY_2^{2-} \rightleftharpoons MXY^{2-} + MY.$$

These reactions can proceed to the right side when a sufficient amount of MX, MY and MY_2^{2-} are available. The circumstances for the formation of MXY^{2-} are from *p*H 3.1 and onwards. In addition to this, there is a decrease in the concentration of MXY^{2-} up to *p*H 3.1. The precise reactions of the changes in the concentrations of MXY^{2-} may be interpreted in the form of its formation equilibria

corresponding to the pH ranges and are as :

$$M^{2+}+HY^{-}+H_2X \rightleftharpoons MHXY^{-}+2H^{+},$$
$$MY+HX^{-} \rightleftharpoons MXY^{2-}+H^{+},$$
$$MX+MY_2^{2-} \rightleftharpoons MXY^{2-}+MY.$$

The potentiometric titration data revealed that three hydrogen ions are liberated during the mixed-ligand formation ; therefore, it is erroneously concluded that the formation of MXY^{2-} takes place by the above mentioned equilibria.

Δlog K values (Table 3) exhibit the same trend as that of UO_2^{2+}-quinolinic-secondary ligands[10] except in the case of UO_2^{2+}-dipicolinic-glutaric acid. The tendency of the mixed-ligand formation is the same in the case of UO_2^{2+}-dipicolinic-succinic, UO_2^{2+}-dipicolinic-itaconic and UO_2^{2+}-dipicolinic-adipic acid ; Δlog K = −0.31, −0.36 and −0.32 respectively. The value of K_{DXY} > 0.6 in UO_2^{2+}-dipicolinic-thiomalic acid system for both the equilibria indicates the additional stabilization of the chelate ring by the neutral sulphur atom in the ternary complex. This effect is greater in the ternary complex than in the corresponding binary one[9]. The reaction constants are higher than 0.6 for UO_2^{2+}-dipicolinic-thiomalic, UO_2^{2+}-dipicolinic-thiodiglycolic and a bit less for UO_2^{2+}-dipicolinic-thiodipropionic acid system. The higher stabilities of the ternary chelates in relation to the binary stabilities is seen in Fig. 1, where MXY^{2-} curve is always above that of MX. In UO_2^{2+}-dipicolinic-thiodipropionic, on the other hand, MXY^{2-} curve in the intermediate pH region drops below MX curve.

The significantly higher values, i.e. 2.67 and 5.07 of K_{DXY} for UO_2^{2+}-dipicolinic-malonic and UO_2^{2+}-dipicolinic-glutaric acid systems respectively accompanied by the higher stability of ternary complexes may be due to very low stabilities of 1 : 2 binary complexes of the secondary ligands. The values of K_{DXY} for the remaining systems for both the equilibria show destabilized nature of ternary complexes. A perusal of all these graphs reveal the concentrations of ternary complexes decrease with increase in pH in the initial stages.

The values of K^{MX}_{MXY} and $K^{MY}_{MY_2}$ indicate the preferential formation of ternary complexes, over the binary except for systems involving the secondary ligands, succinic, itaconic and adipic acids. A comparison of K^{MY}_{MYX} values with $K^{MX}_{MX_2}$ especially in the systems involving malonic and glutaric acid as secondary ligands reveals the preferential formation of corresponding ternary complexes over the binary ones. The order of K^{MY}_{MYX} with reference to the secondary ligands is malonic>glutaric>thiomalic>itaconic>thiodipropionic>succinic>thiodiglycolic>adipic, in accordance with 1 : 1 binary stabilities of these ligands except thiomalic acid[21].

Acknowledgement

Authors are thankful to Prof. M. Santappa, Director, CLRI, Madras, for using the computer programme. Thanks are also due to Prof. K. A. Thakar, Head, Chemistry Department, Marathwada University, Aurangabad for his keen interest. This work is supported by Council of Scientific and Industrial Research, New Delhi.

References

1. H. C. Freeman, J. M. Guss and R. L. Sinclair, *Chem. Commun.*, 1968, 485.
2. E. W. Wilson and R. W. Martin, *Inorg. Chem.*, 1970, **9**, 528.
3. J. V. Rund and K. G. Claus, *Inorg. Chem.*, 1968, **7**, 860 ; 1969, **8**, 59.
4. H. Sigel, '*Metal Ions in Biological Systems*', Marcel Dekker INC, New York, 1973, **2**, 65 ; 1976, **5**, 148, 250.
5. A. Gergely and I. Nagypal, *J. Chem. Soc. Dalton Transactions*, 1977, 1109.
6. P. V. Shelvaraj, *Ph. D. Thesis*, Madras University, Madras, 1974.
7. D. N. Shelke and D. V. Jahagirdar, *Indian J. Chem.*, 1978, **16A**, 60.
8. M. S. Balakrishnan and M. Santappa, *J. Inorg. Nuclear Chem.*, 1974, **36**, 3818 ; 1975, **37**, 1229.
9. P. V. Shelvaraj and M. Santappa, *J. Inorg. Nuclear Chem.*, 1976, **38**, 837 ; 1977, **39**, 119.
10. D. N. Shelke and D. V. Jahagirdar, *J. Inorg. Nuclear Chem.* (In press)
11. S. Ramamoorthy and M. Santappa, *Bull. Chem. Soc.*, Japan, 1968, **41**, 1330.
12. D. N. Shelke and D. V. Jahagirdar, *Bull. Chem. Soc.*, Japan, 1976, **49**, 2142.
13. J. Kirkland, *J. Amer. Chem. Soc.*, 1937, **59**, 1675.
14. H. Irving and H. Rossotti, *J. Chem. Soc.*, 1953, 3397 ; 1954, 2904.
15. S. Ramamoorthy and P. G. Manning, *J. Inorg. Nuclear Chem.*, 1972, **34**, 1977.
16. Y. Marcus and I. Eliezer, *J. Phys. Chem.*, 1962, **66**, 1661.
17. J. I. Watters and R. DeWitt, *J. Amer. Chem. Soc*, 1954, **76**, 3810.
18. A. J. Edward, D. M. Slim, J. E. Guerchais and R. Kergoat, *J. Chem. Soc. Dalton Transactions*, 1977, 1966.
19. D. Rayford, *Diss. Abst. Int. B.*, 1977, **38**, 3189.
20. D. N. Shelke, *Inorganica Chimica Acta*, 1979, **32**, L45.
21. M. Koskinen, *Ann. Acad. Sci. Fenn.*, 1970, **7**, A155.

J. Indian Chem. Soc.,
Vol. LVII, June 1980, pp. 601-603

Studies on Pollutants : A New Reagent for the Determination of Nitrite in Water

(Miss) ALKA BHATT and V. K. GUPTA*

Department of Chemistry, Ravishankar University, Raipur-492 010 (M.P.)

Manuscript received 24 January 1980, accepted 19 May 1980

A new reagent system is described for the micro determination of nitrites in water. The method is based on the reaction of catechol and micro amount of nitrite in 7-8*M* acetic acid and coupling the resultant compound with *p*-aminophenol to form a violet coloured solution. It exhibits a wavelength of maximum absorption at 530 nm. The Beer's law is obeyed from 0.6 ppm to 1.6 ppm. The molar absorptivity and Sandell's sensitivity are found to be 2.3×10^4 litre $mole^{-1} cm^{-1}$ and 0.0023 $\mu g\ cm^{-2}$ respectively.

NITRITES are regarded as one of the important pollutants present in water. Nitrites are formed in water due to microbial oxidation and reduction of ammonia and nitrate. The increasing use of nitrites in foods, fertilizers, detergents and other industries has caused serious pollution problem. Nitrites are considered as potentially hazardous compounds. Nitrites are suspected to cause cancer[1] due to formation of carcinogenic-N-Nitroso compounds by the reaction with secondary or tertiary amines and amides[2]. They also cause the induction of methemoglobinmia[3]. The allowable limits of nitrites in potable water as fixed by U.S. Public Health Service is 0.06 ppm[4]. The determination of nitrites in water in micro amounts is necessary with the view point of pollution studies.

Several methods exist for the detection and determination of nitrite in water. The majority of these lack either specificity or sensitivity. The most widely used methods for the determination of nitrite in water are based on the oxidation of nitrite to nitrate[5-6], the Griess-Ilosvay diazo-reaction[7-10] and the colorimetric reaction with amines[11]. A review of the methods for determination of nitrite is presented by Babko and Pilipenko[12].

In this communication, a new reagent system using catechol and *p*-amino phenol, which has recently been reported[13] for the detection of oxides of nitrogen in air and water, is described for the determination of nitrites in water. The influence of various experimental parameters such as acidity, temperature, amount of reagent, time for maximum colour development, order of addition of reagent, effect of diverse species on the coloured system have been investigated.

Experimental

Apparatus : ECIL spectrophotometer model GS 865 with 1 cm matched cells, was used for all measurements. Graduated apparatus of standard calibration were used for measurements.

Reagents :

(a) *Standard sodium nitrite solution :* A stock solution of sodium nitrite was prepared by dissolving 0.15 g of dried A.R. sodium nitrite in 100 ml glass distilled deaerated water. The standard working solution is obtained by diluting 2 ml of this solution to 100 ml. This solution contains 20 μg nitrite per ml.

(b) *Catechol :* $5 \times 10^{-2} M$ catechol solution was prepared by dissolving 0.55 g of catechol in 100 ml glass distilled water.

(c) p-*Amino phenol :* $1 \times 10^{-2} M$ solution was prepared by dissolving 0.11 g of *p*-amino phenol in 100 ml of 0.1 *M* acetic acid.

(d) *Glacial acetic acid :* 17*M* glacial acetic acid was used as a reaction medium.

(e) *Solutions of foreign species :* These were prepared from analytical reagent grade chemicals.

All the chemicals used were of Analytical Reagent grade. The solution of catechol and *p*-amino phenol were kept in dark and prepared fresh each week.

Colour reaction :

Catechol reacts with nitrite to form nitrosocatechol[14] in acetic acid medium. The nitrosocatechol couples with *p*-amino phenol to give violet colour[15], which is the basis of this method. This complex is extractable in amyl alcohol, butyl alcohol, and isobutyl ketone.

* Senior author to whom correspondence should be made.

Procedure :

An aliquot of sample solution containing not less than 15 μg and not more than 40 μg nitrite was taken in a 25 ml volumetric flask. To it was added 1 ml of catechol and glacial acetic acid and the acidity was maintained $\sim 8M$. The solution was kept for 15 minutes and then 1 ml of *p*-amino phenol was added. Volume was made upto the mark with distilled water. The absorbance of violet coloured solution was measured against the reagent blank prepared under the same condition. The amount of nitrite was deduced from the calibration curve prepared from 15-40 μg of nitrite.

Results and Discussion

Absorption spectrum : The absorption spectrum of the violet coloured species formed by developing colour as described above, was determined in visible region. The absorption spectrum shows that the coloured complex has maximum absorption at 530 nm. The absorbance of the reagent blank was negligible in this region, hence all the measurements were made against distilled water.

Effect of Variables :

Acidity : The wavelength of maximum absorption remains constant from 1-10M acetic acid. Here the acidity was maintained around 7-8M to obtain maximum intensity of the colour. Only acetic acid was found to be suitable for colour development. Other acids change the spectral characteristics and stability of the coloured species.

Effect of time, temperature and reagent concentration : It was observed that at least 15 minutes were required for complete nitrosation and coupling had to be done before 20 minutes after nitrosation. After coupling full colour development takes place in about 45 minutes and is stable for 1 hour.

It was found that the maximum intensity of the colour was obtained at low temperature. The intensity of the colour decreases at higher temperature. Here the temperature was maintained around $20 \pm 2°$. Precaution must be taken that all the measurements are done at the same temperature at which calibration curve is plotted.

The amount of reagent is not critical. For 15-40 μg of nitrite per 25 ml, 1 ml of *p*-amino phenol and 1 ml of catechol solution gave reproducible results.

Order of addition of reagents : It was found that only slight colour developed if catechol was replaced by *p*-amino phenol in the initial reaction.

Beer's law, molar absorptivity and sensitivity :

Beer's law holds good in the range of 15-40 μg of nitrite per 25 ml. The molar absorptivity is 2.3×10^4 lit. mole^{-1} cm^{-1} and Sandell's sensitivity is 0.0023 μg cm^{-2}.

Influence of foreign species :

In order to assess the possible analytical application of the reaction, the effect of several foreign species, present in water were studied. The foreign species were added to a solution containing 20 μg of nitrite and proceeding as recommended in procedure. The results are summarised in the Table 1.

TABLE 1—EFFECT OF FOREIGN SPECIES IN THE DETERMINATION OF NITRITE ION (nitrite 20 μg per 25 ml)

	Species	Added as	Amount added mg	Absorbance at 530 nm
None		—	—	0.84
	Cl^-	NaCl	10	0.84
	SO_4^{2-}	Na_2SO_4	10	0.835
	NO_3^-	$NaNO_3$	2	0.84
	PO_4^{3-}	Na_3PO_4	1	0.84
	NH_4^+	$(NH_4)_2SO_4$	2	0.83
	SO_2	$Na_2S_2O_5$	0.05	0.00
a.	SO_2	,,	0.05	0.83
b.	Cu^{2+}	$Cu(NO_3)_2$	0.5	0.84
b.	Ca^{2+}	$Ca(NO_3)_2$	1	0.845
b.	Mg^{2+}	$MgSO_4$	1	0.84
	Pb^{2+}	$Pb(NO_3)_2$	1	0.84
	V^{5+}	NH_4VO_3	1	0.47
Phenol		as such	40	0.84
Benzene		,,	20	0.84
Aniline		,,	0.02	0.84
Formaldehyde		,,	10	0.83
Nitrobenzene		,,	10	0.84
Ethyl alcohol		,,	20	0.84
Carbon tetrachloride		,,	20	0.84
Chloroform		,,	15	0.835
Aldehyde		CH_3CHO	5	0.84

a. In the presence of 0.5 ml of 0.1N potassium tetrachloro mercurate.

b. In the presence of EDTA as masking agent.

It may however be noted that aniline and sulphur dioxide interfere when present in larger amounts.

The procedure reported is a new approach for the determination of nitrite in water. It has been found that nitrogen dioxide in air can be detected up to 0.6 ppm by absorbing contaminated air through acetic acid solution of catechol and developing the colour as described in the procedure. However due to unreliable absorption efficiency of the acidic absorbing medium, the quantitative estimation of nitrogen dioxide in air is not reliable using phenols[10]. More studies with similar reagents are required to assess the feasibility of this reaction for pollution studies.

Acknowledgement

We are thankful to Professor S. G. Tandon, Head, Department of Chemistry, Ravishankar University, Raipur for providing facilities. One of us (A.B.) is thankful to University Grants Commission, New Delhi, for the award of a Junior Research Fellowship.

References

1. W. Lijinsky and S. Epstein, *Nature*, 1970, **225**, 21.
2. P. Magee and J. Barnes, *Br. J. Cancer*, 1956, **10**, 114.
3. Z. Knotek and P. Schmidt, *Pediatrics*, 1964, **38**, 78.
4. J. E. McKee and H. W. Wolf, Resources Agency of California, "Water Quality Criteria", State Water Quality Control Board Publication, 1963, 3(A), 224.
5. H. Barnes, *Analyst*, 1950, **75**, 388.
6. J. B. Pate and E. C. Tabor, *Amer. Industr. Hyg. Ass. J.*, 1962, **23**, 145.
7. P. Griess, *Chem. Ber.*, 1879, **12**, 427.
8. B. E. Saltzman, *Anal. Chem.*, 1954, **26**, 1949.
9. K. Tori and T. Kiyose, *Anal. Chim. Acta.*, 1977, **88**, 195.
10. T. Nash, *Atmospheric Environment*, 1970, **4**, 661.
11. C. Gelman, B. Ganson and H. Klapper, Proc. 51st Annual Meeting APCA, Phila., Pa. May, 18, p. 1958.
12. A. K. Babko and A. T. Pilipenko, Photometric Analysis, Methods of Determining Non-Metals, (Mir Publishers, Moscow), 1974.
13. A. Bhatt and V. K. Gupta, *Intern. J. of Environ. Stud.*, 1979, **14**, 65.
14. H. Frejka and J. Zika, *Collect. Czech. Chem. Commun.*, 1933, **5**, 253.
15. M. Amarosa and M. R. Cesaroni, *Gazz. Chim. ital.*, 1953, **83**, 853.

J. Indian Chem. Soc.,
Vol. LVII, June 1980, pp. 604-607

Studies on the Molecular Complexes of Para-Benzoquinone and Aminoacids. Part II

A. K. CHATTOPADHYAY and S. C. LAHIRI

Department of Chemistry, University of Kalyani, Kalyani, West Bengal, India

Manuscript received 8 September 1978, revised 24 January 1980, accepted 9 April 1980

Solid compounds of para-benzoquinone (PBQ) with amino acids (glycine, alanine, methionine and arginine) were prepared. Analysis of the data confirms that the composition of the compounds formed between PBQ and aminoacids are generally in the ratio 1 : 2. Efforts have been made to explore the nature of the compounds. The compounds are diamagnetic in character. Solid compounds show marked semiconducting properties, the energy of activation being in the range of 0.88-1.15 ev.

A number of complexes have been reported from the interactions of quinones with aminoacids[1-3]. But controversy exists as to the nature and composition of the complexes whether they are electron-donor acceptor (EDA) complexes or addition reactions[3].

In order to understand the nature of the complexes formed between *p*-benzoquinone and aminoacids, it is desirable to isolate the solid compounds if possible and determine their structure.

Further, studies of amino-quinone[4-8] complexes have indicated that these materials in the solid state have electrical conductivities which are higher than those of the components by 6 to 12 orders of magnitude. It is natural to expect that the aminoacid-quinone compounds may have electrical conductivities and the aspect is worth studying. These studies might provide insight into some of the energy transfer and storage mechanism in biological systems.

We present in this communication the preparation and purification of the solid compounds of *p*-benzoquinone (PBQ) with aminoacids (glycine, alanine, arginine and methionine). Studies on the semiconducting properties of these compounds have also been presented.

Experimental

Purified aminoacid (glycine, alanine, arginine and methionine) in water was added to PBQ in ethanol (appreciably in excess of the stoichiometric amounts). The solution was heated to about 50° and kept for about 50 hours. The solution containing the coloured substance was evaporated under reduced pressure at low temperatures. The compound formed together with large amounts of PBQ and little aminoacid (if any) was repeatedly washed with ether (where only PBQ is soluble) and then with alcohol to remove traces of PBQ and aminoacid (the compound being more soluble in water than alcohol). The compound was then dissolved, dried in vacuum and kept in a desiccator.

The compounds are highly hygroscopic even under ordinary conditions. The elemental analysis of the compounds are given to Table 1.

TABLE 1—ELEMENTAL ANALYSIS OF THE SOLID COMPOUNDS

Compound and m. pt.	Composition	Structure X	Structure Y	$Y+2H_2O$	Found %
PBQ-Glycine	1 : 2	C 47.24	54.05	46.51	47.48
m. pt.		H 3.94	4.50	5.43	4.52
(254-255°)		N 11.02	12.01	10.85	11.05
		O 37.80	28.84	37.21	37.00
PBQ-Alanine	1 : 2	C 51.06	57.60	50.85	49.92
m. pt.		H 4.96	5.60	6.30	5.64
(285-286°)		N 9.98	10.20	9.79	10.32
		O 34.95	25.60	33.56	34.12
PBQ-Methionine	1 : 2	C 47.09	51.38	46.83	47.28
m. pt.		H 6.40	6.95	7.97	7.01
(218-219°)		N 6.90	7.49	6.83	6.91
		O 23.85	17.12	23.86	23.58
		S 15.76	17.11	15.61	15.22
PBQ-Arginine	1 : 1	C 52.38	55.98	91.97	51.10
m. pt.		H 5.56	5.93	6.30	6.30
(234-235°)		N 16.66	17.79	16.54	17.03
		O 25.40	20.45	25.19	25.59

Semiconducting Properties

We could not prepare the single crystals of the solid complexes. The powdered samples were, therefore, placed under the circular jig at pressure of 5 tons/cm². The diameters and widths of the tablets were measured by a microscope. Due to hygroscopic nature of the samples, the samples were protected from moisture by placing them in a tube containing fused calcium chloride even during the measurement of conductivity (Fig. 1).

The establishment of good, stable reproducible electrical contacts between the electrodes and the

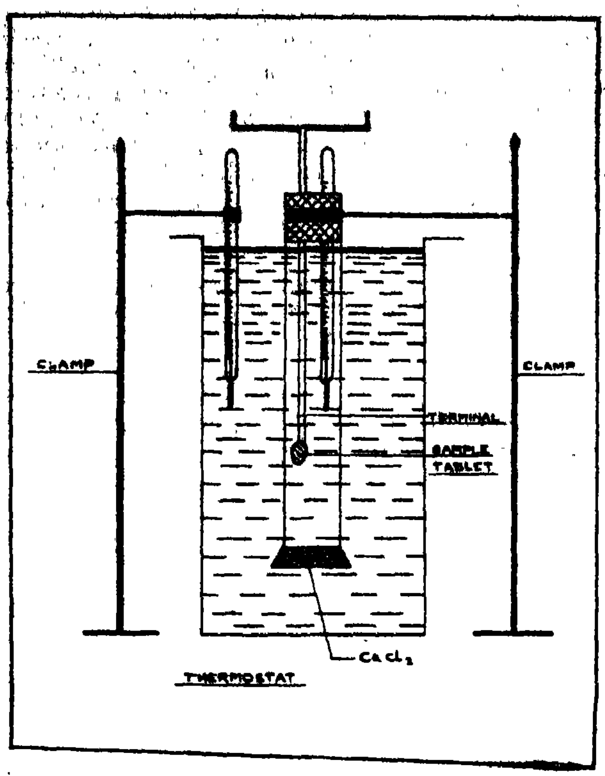


Fig. 1

tablet proved to be difficult. After suitable metallic contacts (with Cu) had been made, the steady increasing voltage from a battery was applied across the samples and the resulting current flow was measured directly in a nanometer. The experiment was repeated at different temperatures. From the V-1 characteristic curves at different temperatures (a typical V-I characteristic curve for alanine-PBQ compound is given in Fig. 2) the resistances (R) and hence the resistivities (ρ) at different temperatures were calculated from the relation

$$R = \rho \frac{\text{length}}{\text{area}}$$

The results are given in Table 2.

TABLE 2—DETERMINATION OF ACTIVATION ENERGY (E)

Compound	Temperature °K	Specific Resistance (ρ) ohm cm^{-1}	Activation Energy E(ev)
PBQ-Glycine	283	2.52 × 10[illegible]	
	290	1.21 × 10[illegible]	0.80
	300	3.98 × 10[illegible]	
PBQ-Alanine	283	9.77 × 10[illegible]	
	290	8.57 × 10[illegible]	0.95
	300	1.00 × 10[illegible]	
PBQ-Methionine	283	6.49 × 10[illegible]	
	290	3.05 × 10[illegible]	1.05
	300	5.13 × 10[illegible]	
PBQ-Arginine	283	4.44 × 10[illegible]	
	290	1.61 × 10[illegible]	1.14
	300	8.00 × 10[illegible]	

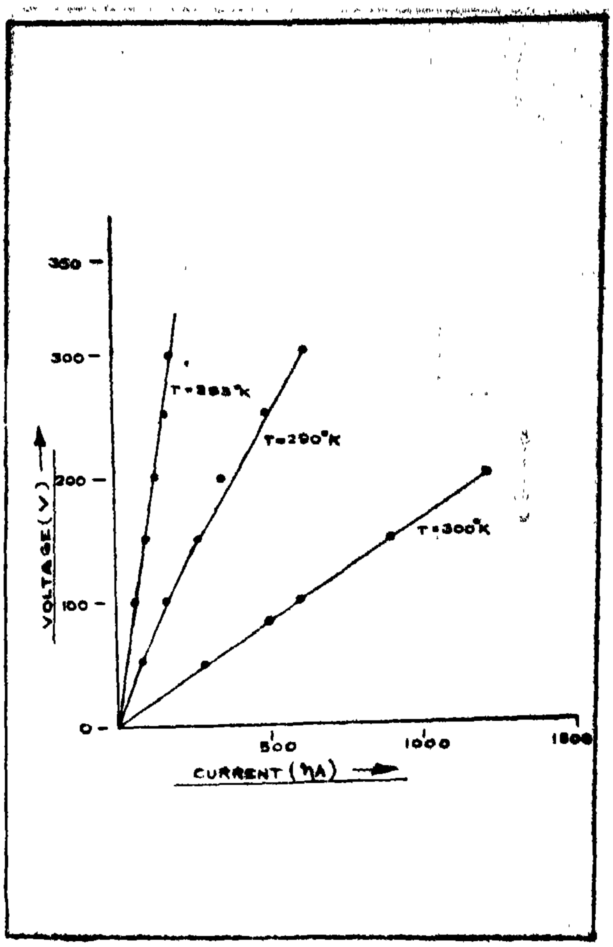


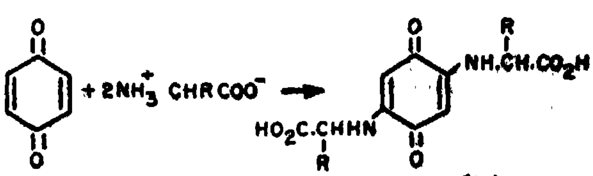
Fig. 2

A typical plot of the specific resistivity versus the reciprocal of the absolute temperature for the alanine-PBQ compound is shown in the Figure 3. The activation energies are given in the Table 2.

Results and Discussion

The nature of the compounds, though interesting is yet not known definitely.

From i.r. studies, Slifkin[1,9,10] infers the compounds to be 1 : 1 C.T. complexes whereas the addition compounds (X) of the type



(X)

have been suggested by Foster[8] similar to the observations made by Woker and Antener[11], Loffe and

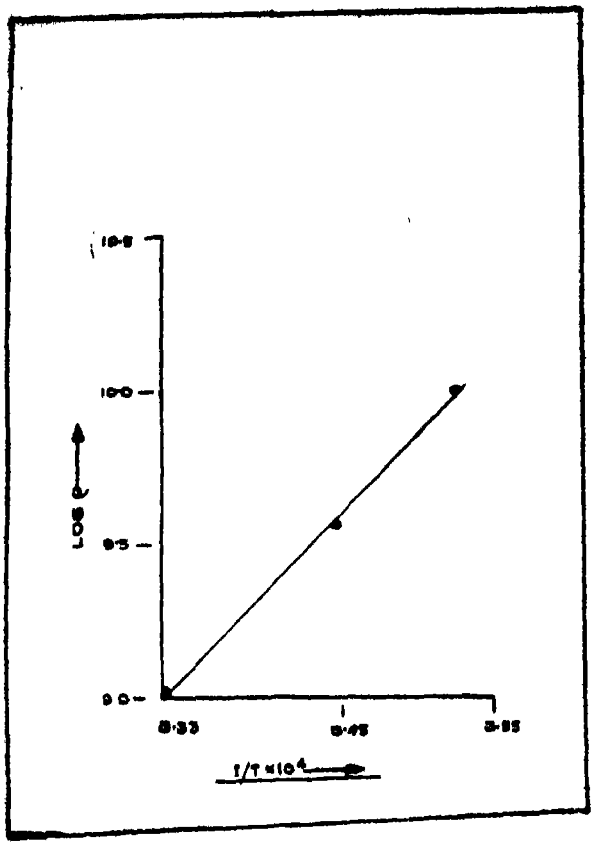
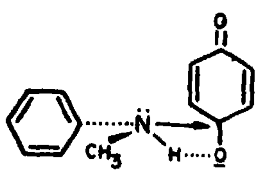


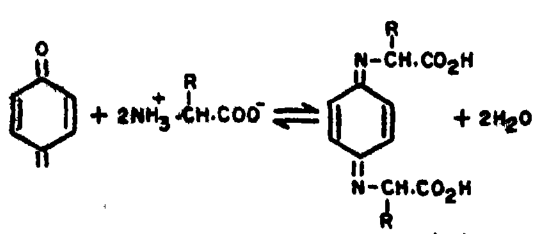
Fig. 8

Khavin[12] and Michalek and Szarkowaka[13]. The structure has been reported to be confirmed by the isolation, purification and identification of (alanine +chloranil) compound from i.r. and n.m.r. studies[8]. From i.r. and polarographic studies, Chattopadhyay *et al*[14] report 1 : 1 C.T. complexes of the type



between PBQ and methylaniline (aniline, *o*-toluidine etc.).

We[15] however, believe that the reaction is



(Y).

similar to Schiff's base type of reaction.

We have isolated and purified the solid compounds from quinone and aminoacids and the analytical data are reported in Table 1. From the results, it is very difficult to suggest which of the structure X or Y is correct. It is seen that the compositions of X and the compositions of $Y+H_2O$ are almost identical. I.R. studies are unable to help us much in this respect. We are unable to adduce further evidence from n.m.r. or mass spectral studies.

The hygroscopic nature of the products, water solubility lead us to believe that the nature of the product is Y rather than X.

All the compounds are diamagnetic in character as observed from magnetic moment measurements but the temperature dependence of magnetic moments could not be measured.

In determining the activation energies of the solid complexes, the equation

$$\rho = \rho_0 e^{-Ea/2RT}$$

used for the intrinsic semiconductors was not applied. Rather, we used the equation

$$\rho = \rho_0 e^{-Ea/RT}$$

as used by Tollin *et al*[8] following the suggestion of Fox[16], where E_a being the activation energy which can be regarded to be the difference between the highest point in the valence band and the lowest point in the conduction band.

The activation energy of the compounds lies between 0.87 ev to about 1.1 ev. The values are close to the values of the activation energies of molecular complexes of flavins and phenols. But the values are considerably higher compared with activation energies which have been obtained in other systems, e.g. 0.019 ev in pyrelene-iodine and 0.15-0.65 ev in the amine-quinone complexes[8].

It is to be noted in this connection that the results are qualitative rather than quantitative as

(a) The protons derived from presence of water of hydration in the solid complex may contribute to the conductivity[17].

(b) The use of powdered sample under high pressure changes the physical state of the samples so as to vitiate the results due to intergranular capacitance and resistance[17,18].

Inspite of the limitations, the conductivity changes can be explained by the removal of the electron from the donor to the acceptor leaving behind a 'hole' into which other electrons may flow similar to the observations of the amino-quinone

complexes in which the 'holes' carry the majority of the current.

It is not known definitely how far these electron-transfer processes are important in biological systems but surely such results can give much insight regarding the electron-transport mechanisms.

Acknowledgement

The authors are thankful to C.S.I.R., Government of India, for a Research Fellowship. The authors express their gratitude to Dr. H. Saha (Department of Physics, Kalyani University) and Late Mr. S. Sengupta for laboratory facilities and help.

References

1. M. A. Slifkin, Charge-Transfer Interactions of Biomolecules, Academic Press, London and New York, 1971.
2. R. Foster, Organic Charge-Transfer Complexes, Academic Press, London, 1970.
3. R. Foster in Molecular Complexes Vol. 2. Ed., R. Foster. Elek Science, London 1974, Chapter 5.
4. D. Bijl, H. Kainer and A. C. Rose—Innes, *J. Chem. Phys.*, 1959, **30**, 765.
5. D. D. Eley, H. Inokuchi and M. B. Willis, *Disc. Faraday. Soc.*, 1959, **28**, 54.
6. R. Sehr, M. M. Labes, M. Bose, H. Ur and F. William, in Electrical Conductivity of Organic Solids, Ed., H. Kallman and M. Silver, Interscience, New York, 1961, 309.
7. M. M. Labes, R. Sehr and M. Bose, *J. Chem. Phys*, 1960, **32**, 1570.
8. A. Roy, A. V. Guzzo and G. Tollin, *Biochim, Biophys. Acta.*, 1965, **94**, 258.
9. M. A. Slifkin and J. G. Heathcoate, *Spectrochim. Acta.*, 1967, **23A**, 2893.
10. M. A. Slifkin and R. H. Walmsley, *Experimentia,* 1969, **25**, 930.
11. G. Woker and I. Antener, *Helv. Chim. Acta.*, 1937, **20**, 1260.
12. I. S. Loffe and Z. Ya. Khavin, *Chem. Abs.*, 1955, **49**, 6169.
13. H. Michalek and L. Szarkowska, *Acta. Biochem. Polon*, 1959, **6**, 399.
14. J. B. Chattopadhyay, M. N. Deshmukh and C. L. Jose, *J. C. S. Farad II*, 1975, **71**, 1127.
15. A. K. Chattopadhyay and S. C. Lahiri, Part I.
16. D. Fox in H. Kallman and M. Silver, Electrical Conductivity in Organic Solids, Interscience, New York, 1961, p. 239.
17. Same as 1, pp 41-42.
18. C. M. Huggins and A H. Sharbaugh, *J. Chem. Phys.*, 1968, **38**, 393.

J. Indian Chem. Soc.,
Vol LVII, June 1980, pp. 608-609

Dipole Moments of Some Non-Benzenoids Calculated by Self-Consistent ω-technique

PRATIP R. RAY, AJAY K. MUKHOPADHYAY and NIRAD G. MUKHERJEE

Department of Pure Chemistry, University College of Science, Calcutta-700 009

Manuscript received 14 February 1979, accepted 19 May 1980

Dipole moments of some non-benzenoids have been calculated by a self-consistent ω-technique. The results obtained are better than those obtained by the conventional ω-technique and are comparable to those obtained by more sophisticated methods.

SOME very interesting analyses have recently been made on the convergence of the ω-technique[1-4]. We have shown earlier that the conventional ω-technique is actually in error[1], and not just slowly convergent as maintained by Harris[4], because of the neglect of the charge dependence of the coulomb integrals while minimising the energy of a system. The neglect of charge dependence during minimization leads to charge distributions which are not strictly self-consistent. In what follows we give the method of self-consistent ω-technique in brief referring elsewhere[1] for further detail and, apply the method for the calculation of dipole moments of some non-benzenoids.

Method of Calculation :

The pi-electron energy (E) of an even electron system is given by $E = 2\mathrm{tr}HR$ ... (1)

where $H_{rr} = \alpha_o + \omega\beta_o(1 - 2R_{rr})$
$H_{rs} = \beta_o$, where r and s are neighbours
$= 0$, otherwise

α_o and β_o are standard coulomb and resonance integrals respectively and ω is a dimensionless constant the value of which is usually taken as 1.4 to provide a best fit with the observed and calculated ionization potentials. The R matrix is defined as equal to TT^+ where the LCAO coefficients of respective MO's are collected in the columns of the T matrix. 2R then gives the charge and bond order matrix.

A first order variation in energy, maintaining the idempotency of R, leads to

$$E = 4\mathrm{tr}\ [(1-R)WR]^+\Delta \quad \ldots (2)$$

where Δ is an arbitrary non-singular matrix and $W = H + D$ with

$$D_{ij} = -2\,\omega\beta_o R_{ij}\,\delta_{ij}$$

At the minimum ($\delta E = 0$), being arbitrary, we have

$$WR = RWR$$

or since $R = TT^+$

$$WT = T(T^+WT) = T\epsilon \quad \ldots (3)$$

which is really Harris' pseudoeigenvalue equation. Diagonalisation of W, however, seldom leads to convergence. This may be, as McWeeny pointed out[5], due to the fact that such an eigenvalue equation uses a wrong energy surface. The change in R corresponding to a steepest descent of the energy surface is given by[1]

$$\delta R = -\lambda L - \lambda^2 LM \quad \ldots (4)$$

where $N = \dfrac{\mathrm{tr}LW}{2(\mathrm{tr}LW - \mathrm{tr}LMW)}$

$L = s + s^+,\ M = s - s^+$

$s = (1-R)WR$, and $N_{ij} = -2\omega\beta_o L_{ij}\delta_{ij}$

The correction leads to the best 1-descent approximation to R and E. The iterative process is continued until self-consistency is achieved. As the convergence of the method seemed very good indeed introduction of any more sophistication like the conjugate gradient technique, etc., into the method is deemed unnecessary. The method thus seems very simple yet promises to give very good charge density distribution.

Results and Discussion

In Table 1 we give the values of dipole moments of some non-benzenoids calculated by the above method along with results obtained by other methods. Experimental values are rare and one has to compare with other theoretical values. As the skeletal formulae of these compounds are simple and wellknown, we avoid depicting them for brevity. We have used the bond-lengths and -angles given by Birss and Dasgupta[6], Dasgupta and Dasgupta[7]

TABLE 1—DIPOLE MOMENTS OF SOME NON-BENZENOID COMPOUNDS (In Debye unit)

Non-Benzenoid	Hückel method	ω-technique	SCF ω-technique	SCF method	Experimental value
1. Fulvene	4.75	2.70	1.96		1.2[x]
2. Azulene	6.41	4.70	1.99	1.79[a] 2.20[b] 2.20[c] 2.74[d]	1.0[x]
3. Acepleiadylene	8.47	6.89	5.30	1.15[a] 2.06[b]	0.5[y]
4. Naphth (cde) azulene	5.98	4.58	3.64	1.71[a] 1.70[b]	—
5. Pentaleno (def) heptalene	5.74	4.45	3.40	1.68[a] 1.51[b]	—
6. Cyclohept (bc) acenaphthylene	4.37	3.47	2.67	0.60[a] 0.87[b]	
7. Cyclohep'a (def) fluorene	10.09	8.10	4.39	4.28[a] 4 00[b] 3.54[c] 4.25[d]	

a : D. H. Lo and M. A. Whitehead—*Canad. J. Chem.*, 1968, **46**, 2027.

b : A. L. H. Chung and M. J. S. Dewar—*J. Chem. Phys.*, 1965, **42**, 756.

c : M. J. S. Dewar and A. J. Harget—*Proc. Roy. Soc. London*, 1970, **A315**, 443, 457.

d : H. Yamaguchi, T. Nakajima and T. L. Kuni, *Theor. Chim. Acta. Berl.*, 1968, **12**, 349.

x : C. W. Wheland and D. E. Mann, *J. Chem. Phys.*, 1949, **17**, 264.

y : D. A. Pitt, A. J. Petro and C. P. Smyth, *J. Amer. Chem. Soc.*, 1957, **79**, 5633.

where the skeletal formulae are also to be found. It has been found that the number of cycles needed for self-consistency for a compound is less than that required in the conventional ω-technique. Harris's method never converged with $\omega = 1.4$ and seldom did so with other values of ω. It is really *gratifying to note that the dipole moment values* calculated by the present method are a lot better than those obtained by Hückel method and conventional ω-technique and in some cases are comparable to those obtained by more sophisticated pi-electron calculations where two electron interactions have been considered. This observation amply justifies our contention that the correct self-consistent charge distributions have been obtained by the present method and hence the dipole moment values are the best possible ones obtainable within the Hückel approximation and for the given geometries.

References

1. P. R. RAY and N. G. MUKHERJEE, *Indian J. Chem.*, 1977, **15(A)**, 144.
2. M. HIDA, Memoirs of Faculty of Technology, Tokyo Metropolitan University, 1974, No. 24.
3. J. GOODISMAN, *Theor. Chim. Acta (Berl.)*, 1974, **36**, 117.
4. F. E. HARRIS, *J. Chem. Phys.*, 1968, **48**, 4027.
5. R. MCWEENY, *Rev. Mod. Phys.*, 1960, **32**, 335.
6. F. W. BIRSS and N. K. DASGUPTA, *Canad. J. Chem.*, 1971, **49**, 2840.
7. A. DASGUPTA and N. K. DASGUPTA, *Canad. J. Chem.*, 1974, **52**, 155.

J. Indian Chem. Soc.,
Vol. LVII, June 1980, pp. 610-612

Studies with Polystyrene Supported Aluminium Ferrocyanide Membranes

W. U. MALIK*, D. K. RASTOGI** and SAT PAUL ARORA

Chemical Laboratories, Mukand Lal National College, Yamuna Nagar-135 001 (Ambala)-India

Manuscript received 12 October 1979, accepted 19 May 1980

Permeability and potential measurements with various electrolytes KCl, KBr, KNO_3, KCNS, K_2SO_4, NaCl, LiCl, $CaCl_2$, $BaCl_2$ and $MgCl_2$ on polystyrene supported aluminium ferrocyanide membrane have been carried out. The results show that the order of permeability for anions is $Cl^- > Br^- > NO_3^- > CNS^- > SO_4^{2-}$ and the order for cations is $K^+ > Na^+ > Li^+$ (1 : 1 electrolytes); $Ba^{2+} > Ca^{2+} > Mg^{2+}$ (2 : 1 electrolytes). Measurement of potential shows an initial increase after which it attains a constant value. The order of membrane potential values for the said anions and cations is reverse of the order of permeability thus indicating the greater the membrane potential, lower the permeability and vice versa. Dynamic response time, fixed charge density and effect of binder percentage on potential have also been reported.

THE literature survey reveals that extensive studies on the membrane behaviour of natural and artificial polymeric membranes[1-3] have been carried out, but the information regarding the relation between the exchange properties and behaviour of synthetic membranes is meagre. Recently Malik and co-workers[4-8] have investigated the measurement of potential and permeability of the membranes prepared from inorganic gels. However, lesser attention has been paid to determine the correlation between ion exchange properties and membrane behaviour of polystyrene supported membranes.

The present communication deals with the measurement of permeability, membrane potential, dynamic response time, fixed charge density and effect of binder percentage of aluminium ferrocyanide membranes.

Experimental

Preparation of the Membranes : Aluminium ferrocyanide gel was prepared by mixing 0.02*M* potassium ferrocyanide (A.R.) solution with 0.04*M* aluminium chloride (A.R.) solution. It was thoroughly washed with double distilled water, filtered, dried and finally sieved into 200 mesh size powder.

Polystyrene supported membranes of aluminium ferrocyanide were prepared[9] by mixing aluminium ferrocyanide gel and polystyrene (50 mesh size powder) in different proportions by weight. The mixture was homogenised in a mortar and 1.5 gm of this mass was put in a die of 2.5 cm diameter. The die was then kept in a specimen mount press and heated gradually upto a temperature of 110° under pressure (6500 to 7000 psi). A large number of membranes containing 15, 20, 25 and 30% of polystyrene were prepared by this method.

Permeability measurements : Permeability measurements were carried out using the Hartung and Willis[10] constant flow method. The membrane under investigation was fitted between two flanges of permeability cell and measurements were carried out by using different electrolytes in the upper half cell. The hydrostatic pressure on each side of the membrane was always kept equal by adjusting the rate of flow of solution and conductivity water across the membrane. The rate of flow of the effluent was kept constant (100±1 ml) per hour. The analysis of the effluent coming out of the lower half cell was made conductometrically. Knowing the rate of flow and concentration of the effluent (coming out of lower half cell), the permeability in millimoles per hour was determined.

Potential measurements : Membranes in their various cationic forms were obtained by dipping them in 1-2*M* solutions of a particular electrolyte for about 48 hours to ensure complete exchange. The membranes were dried completely and cemented to one end of a pyrex glass tube. The tube was inserted in a corked beaker. Solutions of different concentrations of electrolyte were filled in the tube and in the beaker. The membrane potentials were determined indirectly using cells of the type described by Michaelis[11].

SCE ⋮ Solution (C_1) ⋮ Membrane ⋮ Solution (C_2) ⋮ SCE

where $C_1 = 10.C_2$.

* Professor and Head, Chemistry Department, U.O.R., Roorkee (India).

** Department of Chemistry, Meerut College, Meerut (India).

The variation in potential with time was recorded, until potential was maximum. All measurements were made at (25±1°) in a thermostat.

Results and Discussion

The permeability of aluminium ferrocyanide membrane for different electrolytes (Table 1) show that the order of diffusion for anions is $Cl^- > Br^- > NO_3^- > CNS^- > SO_4^{2-}$ and for cations $K^+ > Na^+ > Li^+$ (1 : 1 electrolytes) and $Ba^{2+} > Ca^{2+} > Mg^{2+}$ (2 : 1 electrolytes). It is also clear from permeability data that the rate of permeation of cations is more than anions. This confirms that the membrane is negatively charged and therefore, allows cations more easily to pass through it while anions are not easily passed due to repulsive forces.

TABLE 1—PERMEABILITY OF DIFFERENT ELECTROLYTES ACROSS ALUMINIUM FERROCYANIDE MEMBRANE HAVING 15% BINDER (ELECTROLYTE CONCENTRATION 0.05*M*)

Electrolytes with common cation	Permeability (milli-moles/hour)	Electrolytes with common anion	Permeability (milli-moles/hour)
KCl	0.5070	KCl	0.5070
KBr	0.0624	NaCl	0.1480
KNO_3	0.0582	LiCl	0.1260
KCNS	0.0417	$BaCl_2$	0.0822
K_2SO_4	0.0382	$CaCl_2$	0.0575
—	—	$MgCl_2$	0.0455

The various factors which control electrolyte permeability through a membrane are charge on the membrane, its porosity, the charge and size of the diffusing ion, adsorption, exchange capacity of membrane material and position of the ion in the Hofmeister series.

The fixed charges on the membrane act in two ways. Firstly, these exclude co-ions from the membrane phase due to electrostatic repulsion and secondly increase the mobility of counter ions towards it. The transference of ions through the membrane is also influenced by the size of the hydrated ions. Completely hydrated ions would be less exchangeable than the partially hydrated ones and would consequently show smaller diffusion through the pores of the membrane.

The permeability order for anions $Cl^- > Br^- > NO_3^- > CNS^- > SO_4^{2-}$ is same as their position in the lyotropic series. But the behaviour of SO_4^{2-} ion is altogether different. In this case, the permeability value is very low inspite of the fact that a large electrical driving force should operate due to the two negative charges on the ion. It appears that a very large hydration shell envelopes the ion (evident from the position in the lyotropic series) resulting in the reduction of the electrostatic driving force which will subsequently retard diffusion. It is evident from the data that the sequence for anions is also according to their size. The ions of the smaller size (Cl^- and Br^-) pass through the membrane more easily than bigger ones (NO_3^-, CNS^- and SO_4^{2-}).

The order of diffusion for cations ($K^+ > Na^+ > Li^+$ and $Ba^{2+} > Ca^{2+} > Mg^{2+}$) is opposite to that of their hydrated ionic size. Li^+ (much hydrated) possesses lower permeability values than sodium and potassium (less hydrated). Similarly, Mg^{2+} (much hydrated) possesses lesser permeability than Ca^{2+} and Ba^{2+} (less hydrated). The diffusion rate for cations is also in accordance with the position of the ion in the Hofmeister series.

According to Eisenmann's model[12], the selectivity depends upon the energies of hydration and ion site interaction. The diffusion rates in our case viz. $K^+ > Na^+ > Li^+$ and $Ba^{2+} > Ca^{2+} > Mg^{2+}$ point towards a weak field strength, *i.e.*, normal sequence is followed in case of membranes under investigation.

The potential values (Table 2) due to diffusion of electrolytes through the membrane show that the values for anions are high and for cations are low. This is in good agreement with the fact that higher the potential lower the permeability. The order of potential values for anions is $SO_4^{2-} > CNS^- > NO_3^- > Br^- > Cl^-$ and for cations is $Li^+ > Na^+ > K^+$ (1 : 1 electrolytes) ; $Mg^{2+} > Ca^{2+} > Ba^{2+}$ (2 : 1 electrolytes).

TABLE 2—POTENTIALS OF DIFFERENT ELECTROLYTES OF ALUMINIUM FERROCYANIDE MEMBRANE HAVING 15% BINDER (ELECTROLYTE CONCENTRATION, INSIDE SOLUTION CONCENTRATION/OUTSIDE SOLUTION CONCENTRATION=0.1/0.01*M*)

Electrolytes with common cation	Potentials (mV)	Electrolytes with common anion	Potentials (mV)
KCl	31.4	KCl	31.4
KBr	32.5	NaCl	38.9
KNO_3	33.4	LiCl	49.0
KCNS	33.8	$BaCl_2$	18.5
K_2SO_4	35.4	$CaCl_2$	19.3
—	—	$MgCl_2$	20.1

The method developed by Altug and Hair[13] based on TMS theory was employed to determine the fixed charge density ($w\bar{X}$) of the membrane material where $\bar{X}$ represents the number of ionised sites per unit volume and $w = \pm 1$ depending on the nature of dissociation sites. These E_{TOT} values were plotted against the log of external solution concentration (Fig. 1). The experimental values of membrane potential were also plotted against log concentration of external solution in the same diagram. The theoretical value which coincides with experimental one, gives the value of fixed charge density of the membrane. The fixed charge density of aluminium ferrocyanide is $-0.15N$ at concentration ratio $1.0/0.1M$, $-0.04N$ at concentration

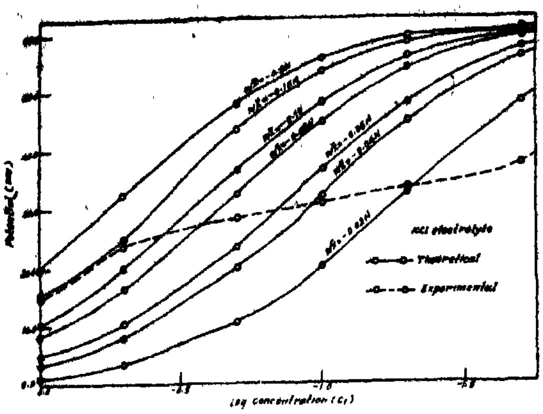


Fig. 1. Membrane potential for different values of fixed charge density.

ratio $0.1/0.01M$ and $-0.02N$ at concentration ratio $0.05/0.005M$. These studies show that fixed charged density is not a constant quantity but depends upon the concentration of the solution separating the membrane.

The dynamic response time of membrane electrode was determined by recording the resulting potential versus time (Fig. 2) for different concentrations of electrolyte (keeping $C_1 = 10.C_2$). The highest peak of the curve gives the equilibration time which is about 500 seconds for this membrane. This equilibration time is almost negligible as compared to other ion-selective electrodes and is probably due to its semi-crystalline nature.

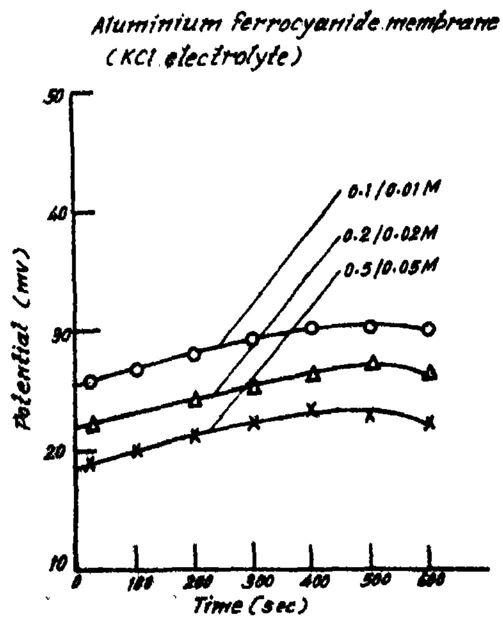


Fig. 2. Dynamic response time of membrane electrode.

The effect of concentration of binder on the membrane behaviour was investigated in the range 15 to 30% (Table 3). The effect of concentration of binder on membrane behaviour was not investigated in the membranes having less than 15% polystyrene owing to their instability and more than 30% polystyrene owing to separation of exchange particles by the binder. It was, therefore, concluded that the π-electrons of the binder do not affect the electrochemical behaviour of the exchanger at least in these concentration ranges. However, possibility of this factor influencing the membrane behaviour in dilute solutions cannot be completely ignored.

TABLE 3—POTENTIALS OF ALUMINIUM FERROCYANIDE MEMBRANES HAVING VARYING AMOUNTS OF BINDER (ELECTROLYTE CONCENTRATION = 0.1/0.01M)

Electrolytes	Observed potentials (mV) in the membranes having			
	15% binder	20% binder	25% binder	30% binder
LiCl	49.0	49.1	49.1	49.2
NaCl	33.9	33.8	33.9	34.0
KCl	31.4	31.5	31.4	31.6
KBr	32.5	32.7	32.6	32.6
KNO_3	33.4	33.4	33.5	33.5
KCNS	33.8	33.7	33.8	33.7
K_2SO_4	35.4	35.5	35.6	35.6
$MgCl_2$	20.1	20.1	20.0	20.1
$CaCl_2$	19.8	19.9	20.0	19.8
$BaCl_2$	18.5	18.5	18.6	18.5

Acknowledgement

The authors thank Principal T. R. Chadha, M. L. N. College, Yamuna Nagar for providing facilities and to U. G. C. (India) for the award of financial assistance to one of them (S.P.A.).

References

1. T. TEORELL, *Disc. Faraday Soc.*, 1956, **21**, 9.
2. H. J. ZWOLINSKY, *J. Phys. Chem.*, 1949, **53**, 1426.
3. A. J. MEACKIE and P. MEARS, *Proc. Roy. Soc.*, 1955, **A-232**, 498.
4. W. U. MALIK and F. A. SIDDIQI, *J. Colloid Sci.*, 1963, **18**, 161.
5. W. U. MALIK and S. A. ANWAR, *Indian J. Chem.*, 1965, **3**, 491.
6. W. U. MALIK and H. ARIF, *Bull. Chem. Soc., Japan*, 1967, **40**, 1746.
7. W. U. MALIK, S. K. SRIVASTAVA, V. M. BHANDARI and SATISH KUMAR, *J. Colloid Interface Sci.*, 1974, **47**, 1.
8. W. U. MALIK, S. K. SRIVASTAVA, R. K. GULATI and SAT PAUL ARORA, *J. Electrochem. Soc. India*, 1977, **26**, 3.
9. M. R. J. WYLLIE, *J. Phys. Chem.*, 1950, **54**, 204.
10. G. M. WILLIS, A. T. AUSTIN and E. J. HARTUNG, *Trans. Faraday Soc.*, 1944, **40**, 520.
11. MICHAELIS, *Kolloid-Z*, 1963, **62**, 1.
12. G. EISENMANN, *Biophys. J. Suppl.*, 1962, **2**, 259.
13. J. ALTUG and M. L. HAIR, *J. Phys. Chem.*, 1968, **72**, 599.

J. Indian Chem. Soc.,
Vol. LVII, June 1980, pp. 613-616

Solute-Solvent Interactions. Part I. Viscosity of Sodium Acetate in Acidic Aqueous Ethanol

K. GANAPATHY and M. RAMANUJAM

Department of Chemistry, Annamalai University, Annamalainagar, 608 101

Manuscript received 19 November 1979, revised 10 March 1980, accepted 13 May 1980

The viscosity of the solution of sodium acetate in acidic aqueous ethanol (10-90% v/v) has been measured at 30°. The viscosities at 30°, 35° and 40° have also been measured for different concentrations of sodium acetate in 50% ethanol. The energy of activation for the viscous flow for different compositions of the salt is given. The viscosity data have been fitted to Jones-Dole equation. The B-coefficient increases with increasing temperature which indicates that sodium acetate behaves as a structure breaker in acidic aqueous ethanol. From the density measurements it is found that the Root's equation is valid only in the lower concentration of sodium acetate in this medium.

AMONG the various methods to study the solute-solvent interactions, that which involves viscous and density data is easier and simpler. The B-coefficient of Jones-Dole equation[1] is a better measure of the interaction of the added electrolyte in a particular medium. This is in accordance with the views of Gurney[2], Kaminsky[3] and Nightingale[4]. To know the effect of solvent on the polarographic parameters such as diffusion current, half-wave potential and polarographic maxima (the study of which is in progress), the nature of composition, interaction and solvent structure are needed. Hence in the present study viscosities of solutions of sodium acetate (supporting electrolyte) in the solvent composed of water, ethanol, 0.03% gelatin (maximum suppressor) and 0.1 *N* acetic acid (for buffer action) have been measured. Only the composition of ethanol and water is varied keeping the concentration of gelatin and acetic acid constant throughout.

Experimental

Sodium acetate (Analar grade) was used as such. Acetic acid was purified over chromium trioxide. Doubly distilled water was used for preparing various solutions. Gelatin was used without further purification. The viscosity was measured with an Ostwald's viscometer and the density of the solutions using a specific gravity bottle (10 ml capacity). The viscosity coefficients of water used for calculation were 0.8004, 0.7208 and 0.6536 at 30°, 35° and at 40° respectively.

Results and Discussion

The viscosity of sodium acetate in the solvent composed of 10-90% (v/v) ethanol, water, 0.03% gelatin and 0.1 *N* acetic acid in the concentration range (0.0060 to 0.4*M*) were determined. The viscosity of sodium acetate decreases in the lower concentration and increases with the increase of salt concentration. As the ethanol content of the solvent is increased the viscosity increases first and decreases above 70% of ethanol. With increase in temperature decrease of viscosity is observed. The viscosity data have been analysed by means of Jones-Dole equation (1)

$$\eta/\eta_0 = 1 + A\sqrt{C} + BC \qquad \ldots \quad (1)$$

where η is the viscosity of the solution. η_0 is the viscosity of the solvent, C is the molar concentration and A and B are constants characteristic of the solute electrolyte. The values of A and B of equation (1) are determined from the intercept and slope of the linear plots of $(\eta/\eta_0 - 1)/\sqrt{C}$ vs $\sqrt{C}$. The plots in all the cases of acidic aqueous ethanol are shown in Fig. 1.

In the Jones-Dole equation A denotes ion-ion interaction and B denotes solute-solvent interaction. In general, the magnitude of A value for common salts appears to be smaller. The A values obtained are negative upto 60% of ethanol content and above 60%, it is positive upto 90% of ethanol content. The value of A increases as the temperature is increased. However, the interpenetration effect (cation-cation[5-8]) and (cation-anion[8,9]) which also brings ions together, may be responsible for the increase. The value of A should decrease with rise in temperature which one should expect in view of more violent thermal agitation at higher temperature and reduction of attractive forces. Since A is a measure of ion-ion interaction which assumes significance in very dilute solutions and data reported here are for higher concentrations it would be unwise to make further comments on these values.

B values for sodium acetate is positive in all compositions of the solvent studied here. It may

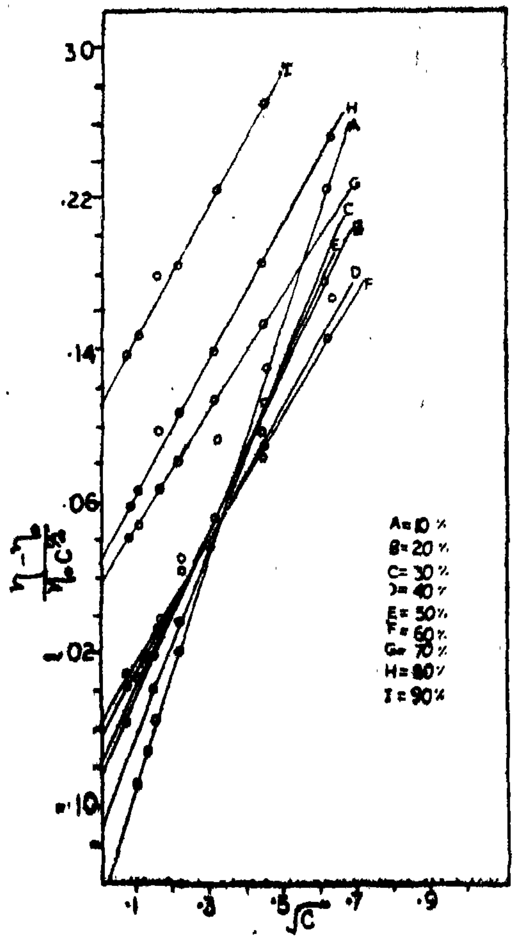


Fig. 1

TABLE 2—THE VALUES OF THE PARAMETERS A AND B OF JONES-DOLE EQUATION

Composition of ethanol%	A	B
10	−0.144	0.5882
20	−0.086	0.4000
30	−0.122	0.4820
40	−0.062	0.3438
50	−0.054$_a$	0.3281
	−0.041$_b$	0.3280
	−0.082$_c$	0.3338
60	−0.078	0.4787
70	0.016	0.2880
80	0.026	0.3555
90	0.1081	0.3535

(a) denotes at 30°,
(b) denotes at 35°,
(c) denotes at 40°.

be noted from Table 2 that the variation of B value with composition of the solvent is not regular indicating that the electrostatic ion-solvent interaction varies with the behaviour of gelatin with the alcohol and acidic content of the medium. The high charge density on the small cation gives rise to strong electrostatic interaction in solution, i.e., the smaller the ion, the stronger the ion-solvent dipole interaction and hence larger the size of the solvated ion in solution. The irregularity in variations of B value may be due to the degree of hydrolysis of gelatin since it is in acid medium. The positive temperature coefficient of B, dB/dT suggests that the salt behaves as a structure breaker in this case. The effect of addition of ethanol in water has been deduced from the viscosity data of binary mixtures of water and ethanol. Viscosity data for binary mixtures have yielded information regarding the nature of the interactions[10,11]. For the viscosity of such binary mixtures we have used equation (2) suggested by Grunberg and Nissan[12].

$$\ln \eta_{mix} = X_1 \ln \eta_1 + X_2 \ln \eta_2 + X_1 X_2 d \quad \ldots \quad (2)$$

where η_{mix} is the viscosity of the mixture, η_1 is of the liquid one, η_2 of the liquid second. X_1 and X_2 are the mole fractions of the component of the mixture. d is proportional to w/RT and w is the interchange energy. The parameter has the same significance as given by Guggenheim[13] in the treatment of regular solution theory and d has been regarded as a better measure of the strength of interaction between the components in solution. The data for d along with excess viscosity and energy of activation are given in Table 3. (i) If $\eta^E > 0$, $d > 0$ and the magnitude of both is large, then strong specific interaction would be present. (ii) If $\eta^E < 0$ but $d > 0$ then weak specific interaction would be present[14] and (iii) if $\eta^E < 0$ and $d < 0$ and the magnitude of both is larger, then specific interaction would be absent. In the present case $\eta^E > 0$, $d > 0$ and the magnitude of both is large at all compositions and temperature (except at 40° where d is negative for the 0.0731 mole fraction of ethanol) suggesting strong specific interactions.

According to Stokes and Mills[15] the viscosity of electrolytic solution incorporates that of solvent plus the contribution from four other sources. Thus

$$\eta = \eta^0 + \eta^+ + \eta^A + \eta^E + \eta^D \quad \ldots \quad (3)$$

where η^+ is the positive increase in viscosity caused by long range electrostatic interaction; η^E is the positive increase due to the shape and size of an ion, η^A is the increase due to alignment or orientation of the polar molecules by the ionic field and η^D is the decrease in viscosity arising due to the distortion of the solvent structure by the ions. Substituting equation (3) in (1) and eliminating the

contribution due to the Coulombic interaction from both, we get

$$\eta^E+\eta^A+\eta^D=\eta^0 BC$$

Therefore B-coefficient can be discussed in terms of these viscosity effects at a particular concentration and temperature.

The sodium ion having high charge density strongly orient solvent molecules making a sheath of firmly attached layer. The positive and larger value of B-coefficient may be attributed to the strong association between water and ethanol through multiple hydrogen bonding. Thus the solvated ions would lead to larger values of η^E and η^A. This argument holds good for the ions of intermediate size like Na^+ for which $\eta^E+\eta^A \approx \eta^D$. It may be observed from Table 1 that the temperature coefficient of viscosity at 50% ethanol increases with increasing concentration of sodium acetate and decrease with rise in temperature as one should expect in view of the larger value of η at higher concentrations and low temperature. The effect of temperature on the viscosity is given by

$$\eta = Ae^{E\eta/RT}$$

where A is a constant, $^E\eta$ is the activation energy for the viscous flow and other symbols have usual significance. The plots of log η versus 1/T for different concentrations of sodium acetate in 50% ethanol are linear. $^E\eta$ values were obtained from the slope of the plots and are given in Table 4. The energy of activation for ethanol water system has also been given in Table 3. $^E\eta$ can be related to the work needed to form vacant sites[16] in the solvent matrix and may be regarded as the measure of the structure of the solvent.

TABLE 1—VISCOSITY OF SODIUM ACETATE IN ACIDIC AQUEOUS ETHANOL

Molarity	η (cp)	$\frac{\eta-\eta_0}{\eta_0}$	$\frac{\eta-\eta_0}{\eta_0 C^{1/2}}$
50% ethanol + water + 0.03% gelatin + 0.1*N* Acetic acid			
0.0000	1.9196(a)	—	—
	1.6067(b)		
	1.3688(c)		
0.0062	1.8976(a)	−0.0115	−0.0322
	1.6046(b)	−0.0013	−0.0167
	1.3615(c)	−0.0053	−0.0046
0.0125	1.9001(a)	−0.0028	−0.0247
	1.6056(b)	−0.0007	−0.0064
	1.3640(c)	−0.0035	−0.0318
0.0250	1.9080(a)	−0.0009	−0.0063
	1.6097(b)	0.0019	0.0121
	1.3711(c)	0.0029	0.0182
0.0500	1.9252(a)	0.0029	0.0130
	1.6197(b)	0.0081	0.0362
	1.3789(c)	0.0074	0.0331
0.1000	1.9490(a)	0.0153	0.0483
	1.6376(b)	0.0192	0.0607
	1.4000(c)	0.0229	0.0725
0.2000	1.9877(a)	0.0355	0.0795
	1.6806(b)	0.0460	0.1029
	1.4362(c)	0.0492	0.1100
0.4000	2.0955(a)	0 0916	0.1448
	1.7660(b)	0.0991	0.1569
	1.5059	0.1001	0.1583

(a) denotes at 30°, (b) denotes at 35°, (c) denotes at 40°.

TABLE 3—VISCOSITY DATA OF DIFFERENT AQUEOUS MIXTURES OF ETHANOL

Mole fraction of Ethanol	Excess Viscosity η^E	d	Energy of activation $^E\eta \times 10^{-3} JM^{-1}$
Ethanol	—	—	3.47
0.0731	0.4674(a)	6.5750	
	0.3577(b)	5.8695	4.63
	0.2861(c)	−0.0974	
0.1738	0.8874(a)	3.4779	
	0.6983(b)	4.5197	4.73
	0.5752(c)	4.2356	
0.3213	0.9742(a)	3.3834	
	0.7792(b)	3.1275	6.94
	0.6342(c)	2.8954	
0.5580	0.6836(a)	2.1651	
	0.5535(b)	2.0159	7.29
	0.4539(c)	1.8688	

(a) denotes at 30°,
(b) " 35°,
(c) " 40°.

TABLE 4—ENERGY OF ACTIVATION FOR THE VISCOUS FLOW OF SODIUM ACETATE IN 50% ETHANOL

Molarity	$^E\eta \times 10^{-3} JM^{-1}$
0.0000	5.61
0.0062	3.95
0.0125	6.03
0.0250	4.79
0.0500	5.54
0.1000	6.41
0.2000	7.15
0.4000	8.42

Densities of the salt solutions in acidic aqueous ethanol at different compositions of alcohol have been found to fit the Root's equation[17] (4) only in the lower concentrations. As the concentration increases some deviation is observed.

$$d = d_0 + AC - BC^{3/2} \quad \ldots (4)$$

where A and B are constants specific to salt and d and d_0 are densities of salt solution and pure solvent respectively. On transforming equation (4) we get equation (5)

$$\frac{d-d_0}{C} = A - B\sqrt{C} \quad \ldots (5)$$

Thus a plot of $\frac{d-d_0}{C}$ versus $\sqrt{C}$ should be linear with A = intercept and B = slope of the plot. The values of the constants A and B of equation (4) estimated from these plots are given in Table 5.

TABLE 5—THE VALUES OF THE PARAMETERS A AND B OF ROOT'S EQUATION

Composition of Ethanol%	A	B
10	0.119	0.2000
20	0.187	0.5125
30	0.292	1.0267
40	0.415	1.3571
50	0.190	0.2400
60	0.275	0.9000
70	0.240	0.7400
80	0.545	0.2500
90	0.341	−0.4267

Acknowledgement

The authors are thankful to the University Grants Commission, New Delhi, for the award of a Junior Research Fellowship to one of them (M.R.).

References

1. G. JONES and M. DOLE, *J. Amer. Chem. Soc.*, 1929, **51**, 2950.
2. R. W. GURNEY, Ionic Processes in Solution (McGraw-Hill, New York), 1953.
3. M. KAMINSKY, *Disc. Faraday Soc.*, 1957, **24**, 171.
4. E. R. NIGHTINGALE (Jr.) and R. F. BRUCK, *J. Phys. Chem.*, 1959, **63**, 1777.
5. W. Y. WEN and K. NARA, *J. Phys. Chem, Ithaca*, 1967, **71**, 2149.
6. R. H. WOOD and H. L. ANDERSON *et al.*, *J. Phys. Chem.*, 1967, **71**, 2149.
7. R. A. HARNE and R. P. YOUNG, *J. Phys. Chem. Ithaca*, 1968, **72**, 1768.
8. R. GOPAL and K. SINGH, *Z. Phys. Chem. Frank. Ausg.*, 1970, **69**, 81.
9. S. R. C. HUGHES and D. H. PRICES, *J. Chem. Soc.* (A), 1967, 1093.
10. LILER and KOSANOVIC, Hydrogen Bonding, edited by Hadzi (Pergamon Press, London), 1959, p. 529.
11. J. M. G. GOIVIR and P. M. TOPOROWSNI, *Canad. J. Chem*, 1961, **39**, 2240.
12. L. GRUNBERG and A. H. NISSAN, *Nature*, (Lond.), 1949, **164**, 799.
13. E. A. GUGGENHEIM, Mixtures (Oxford University Press, London), 1952.
14. I. BROWN and W. FOCK, *Aust. J. Chem.*, 1957, **10**, 417.
15. R. H. STOKES and R. MILLS, The International Encyclopaedia of Physical Chemistry and Chemical Physics, 1965, Vol. 3, 89.
16. A. FINDLAY, Practical Physical Chemistry (Longmans, Green, London), 1967, p 87.
17. W. C. ROOT, *J. Amer. Chem. Soc.*, 1933, **55**, 850.

J. Indian Chem. Soc.,
Vol. LVII, June 1980, pp. 617-619

Carbon-Nitrogen-Sulphur Relationships in Soils of West Bengal

PARTHA MUKHOPADHYAY and ASIT K. MUKHOPADHYAY

Department of Agricultural Chemistry and Soil Science, Bidhan Chandra Krishi Viswa Vidyalaya, Kalyani, Nadia, W. Bengal

Manuscript received 19 July 1979, revised 11 February 1980, accepted 9 April 1980

Carbon, nitrogen and sulphur relationships were studied in twelve profiles from five soil zones of West Bengal. Considerable variability in C : N, C : S, N : S and C : N : S ratios were observed in soils of different regions. Mean C : S and N : S ratios of the soil increased in the order : Coastal Saline ⩽ Lateritic < Alluvial << Hill < Terai. N : S ratio of surface soils were higher than the sub-surface layers. Presence of variable proportion of different components of organic matter in the soil under the influence of different climatic factors is suggested.

MOST of the sulphur, nitrogen and carbon in arable soils are present in organic forms. However, the importance of sulphur was overlooked in the earlier periods because of its incidental application as a constituent along with nitrogenous and phosphatic fertilizers. But the increased use of high analysis sulphur-free fertilizers, decreased use of sulphur as pesticides, introduction of high yielding varieties of crops which means greater requirement of all essential nutrients and decreased contribution of sulphur from atmospheric sources as a result of comparatively less combustion of sulphur containing fuels resulted in reports of more frequent and widespread sulphur deficiency in soils.

Considerable work has been done on the distribution of sulphur and its relationship with carbon and nitrogen in organic fraction in soils of many other states of India (Kanwar and Mohan[1], Kanwar and Takkar[2], Ahamed and Jha[3], Venkateswarlu *et al*[4], Virmani and Kanwar[5], Bhan and Tripathi[6] and Kumar and Singh[7]). But inspite of the reported deficiency of sulphur in soils of West Bengal (Dutta[8,9]) so far no systematic effort on this aspect has been made on soils of this state. Moreover, most of the previous works on sulphur of different regions of India have been limited to surface soils and not in the zone of root penetration. This knowledge is obviously important for interpreting soil tests and fertilizer response to sulphur by deep rooting crops. The present paper therefore reports an examination of the vertical distribution of organic sulphur and its relationship with organic carbon and total nitrogen in soils of different regions of West Bengal.

Experimental

Twelve soil profiles from five regions (namely, Hill, Terai, Lateritic, Alluvial and Coastal Saline) of West Bengal were selected for the present investigation. Soils were collected from three different depths viz., 0-15 cm, 15-30 cm and 30-45 cm layer in each profile. Samples were air-dried and crushed to pass through 0.5 mm sieve.

In the soil analyses reported (Table 1) *p*H was determined with a glass electrode *p*H meter (Soil : Water 1 : 2.5), organic carbon by wet digestion method of Walkely and Black (Jackson[10]) and total nitrogen by a semi-micro Kjeldahl method (Bremner[11]). Total sulphur was determined by the method of Bardsley and Lancaster[12] and organic sulphur was calculated by subtracting inorganic sulphur from total sulphur. The concentrations of sulphur in the extracts were determined by the reduction method of Johnson and Nishita[13].

Results and Discussion

Organic carbon, total nitrogen and organic sulphur contents in the soils (Table 1) and computed C : N, C : S, N : S and C : N : S ratios are presented in Table 2. The data presented in Table 1

TABLE 1—ANALYSES OF SOIL PROFILE SAMPLES

Region	Place of collection	Depth (cm)	*p*H	%Org. Carbon	%Total Nitrogen	%Org. Sulphur
	Ambutia,	0-15	4.35	3.20	0.416	0.0256
	Kerseung	15-30	4.25	1.57	0.210	0.0212
		30-45	4.10	2.06	0.290	0.0206
Hill	Mundabasti,	0-15	4.90	3.14	0.424	0.0218
	Darjeeling	15-30	4.65	2.59	0.384	0.0211
		30-45	4.70	2.27	0.380	0.0198
	Kalimpong	0-15	5.80	2.28	0.212	0.0178
		15-30	5.65	1.45	0.158	0.0115
		30-45	5.65	1.27	0.138	0.0110
	Ektiasal,	0-15	5.15	2.28	0.258	0.0107
	Jalpaiguri	15-30	5.65	1.80	0.219	0.0105
Terai		30-45	5.40	1.20	0.156	0.0069
	Mohitnagar	0-15	5.50	2.38	0.261	0.0162
		15-30	5.20	2.82	0.236	0.0164
		30-45	5.20	2.69	0.224	0.0165

(Table 1 Contd.)

Lateritic	Raghunathpur	0-15	5.05	0.69	0.068	0.0091
		15-30	5.50	0.27	0.021	0.0058
		30-45	6.95	0.08	0.006	0.0018
	Sreeniketan	0-15	5.85	0.23	0.024	0.0044
		15-30	5.55	0.21	0.019	0.0045
		30-45	5.50	0.09	0.008	0.0024
Alluvial	Burdwan	0-15	6.05	0.36	0.037	0.0068
		15-30	6.95	0.27	0.025	0.0095
		30-45	6.70	0.10	0.009	0.0081
	Chinsurah	0-15	6.00	0.77	0.071	0.0050
		15-30	7.60	0.42	0.037	0.0051
		30-45	8.43	0.17	0.014	0.0080
	Mondouri	0-15	6.10	0.86	0.089	0.0084
		15-30	6.50	0.41	0.042	0.0045
		30-45	7.20	0.45	0.058	0.0072
Coastal Saline	Mathurapur	0-15	5.70	0.54	0.053	0.0081
		15-30	7.00	0.40	0.036	0.0066
		30-45	7.62	0.38	0.032	0.0064
	Canning	0-15	7.45	0.73	0.077	0.0116
		15-30	8.10	0.49	0.047	0.0120
		30-45	8.10	0.46	0.047	0.0078

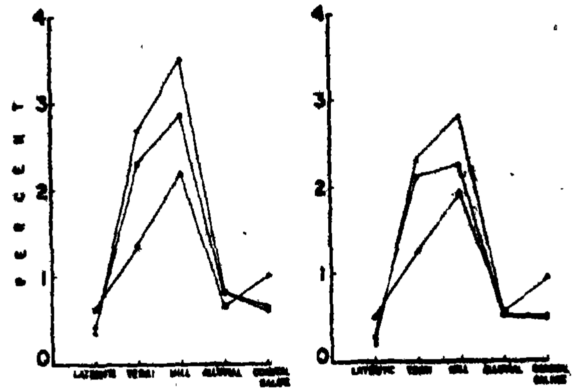
TABLE 2—CARBON, NITROGEN AND SULPHUR RELATIONSHIPS IN SOILS

Region	Place of collection	Depth (cm)	C : N	N : S	C : S	C : N : S
Hill	Ambutia, Kerseung	0-15	7.7	16.2	125.1	77 : 10 : 0.61
		15-30	7.4	9 9	74.4	74 : 10 : 1 00
		30-45	7.1	14.1	99.9	71 : 10 : 0.71
	Mundabasti, Darjeeling	0-15	7.4	19.4	144.0	74 : 10 : 0.51
		15-30	7.7	15.8	122.7	77 : 10 : 0.63
		30-45	6.9	16.6	114.6	69 : 10 : 0.60
	Kalimpong	0-15	10.5	11.9	126.0	105 : 10 : 0.83
		15-30	9.1	10.2	93.6	91 : 10 : 0.98
		30-45	9.2	12.5	115.4	92 : 10 : 0.80
Mean			7.8	14.5	114.0	78 : 10 : 0.68
Terai	Mohitnagar	0-15	8.8	17.3	148.8	88 : 10 : 0.57
		15-30	9.8	14.4	141.4	98 : 10 : 0.70
		30-45	12.0	13.5	168.2	120 : 10 : 0.73
	Ektiasal, Siliguri	0-15	8.8	24.1	218.6	88 : 10 : 0.41
		15-30	8.2	20.8	171.9	82 : 10 : 0.48
		30-45	7.7	22.6	292.6	77 : 10 : 0 26
Mean			9.2	17.9	164.0	92 : 10 : 0.54
Lateritic	Raghunathpur	0-15	10.1	8.4	65.8	101 : 10 : 1.10
		15-30	12.8	8.9	50.9	128 : 10 : 2.50
		30-45	12.7	3.6	46.4	127 : 10 : 2.70
	Sriniketan	0-15	9.7	5.4	52.9	97 : 10 : 1.80
		15-30	11.1	4.2	47.1	111 : 10 : 2.30
		30-45	10.3	3.5	40.0	103 : 10 : 2.85
Mean			10.7	5.5	59.4	107 : 10 : 1.81
Alluvial	Burdwan	0-15	9.8	5.9	57.6	98 : 10 : 1.70
		15-30	11.0	2.6	29.6	110 : 10 : 3.70
		30-45	11.8	2.9	33.9	118 : 10 : 3.40
	Chinsurah	0-15	10.9	14.5	157.9	109 : 10 : 0.69
		15-30	11.4	7.2	83.1	114 : 10 : 1.37
		30-45	12.3	4.6	57.6	123 : 10 : 2.14
	Mondouri	0-15	9.7	10.7	103.7	97 : 10 : 0.93
		15-30	9.7	9.5	92.7	97 : 10 : 1.04
		30-45	7.8	8.0	63.3	78 : 10 : 1.24
Mean			10.0	7.4	73.4	100 : 10 : 1.36
Coastal Saline	Mathurapur	0-15	10.2	6.6	68.0	102 : 10 : 1.50
		15-30	11.1	5.4	60.4	111 : 10 : 1.83
		30-45	10 3	5.0	52.3	103 : 10 : 1.96
	Canning	0-15	9.4	6.6	63.3	94 : 10 : 1.50
		15-30	10.4	3.9	41.1	104 : 10 : 2.58
		30-45	9.9	6.3	62.7	99 : 10 : 1.59
Mean			10.1	5.6	56.4	101 : 10 : 1.78
12 [illegible] e soils		0-15	8.6	14.0	120.9	86 : 10 : 0.71
[illegible]		0-45	8.9	11.9	106.2	89 : 10 : 0.81

reveal that organic sulphur content of the surface horizons of the soil profiles examined varied from 18 to 256.7 ppm. Average organic sulphur content of Hill and Terai regions (189.6 and 124.3 ppm respectively) was noticeably higher than that observed in soils of Lateritic, Alluvial and Coastal Saline regions (average being 44.27, 57.81 and 86.85 ppm respectively). This was so because the organic matter contents of the soil profile of Hill and Terai region were higher than those of the other regions. It is also evident that the sulphur content showed a general decline with depth in the case of soils of acidic and neutral reaction, whereas, in soils of alkaline reaction no such regular decrease in sulphur content was observed. This is due to the fact that most of the soil sulphur present in neutral and acidic soils is primarily organic in nature. While in the case of saline soils the non-organic forms dominate (Mukhopadhyay and Mukhopadhyay[14]). But for the soils of Coastal Saline region, the organic sulphur decreased with depth. Organic matter also decreased with depth. Consequently organic sulphur which is also a constituent of soil organic matter also decreases. Similar trends were also reported by Venkateswarlu *et al*[4].

The organic carbon to total nitrogen values for the fairly non-calcareous soils fall in the range of 7.1 to 12.8. These differences show little relationship with the present *p*H but they are readily understood on the basis that the C : N ratio indicates the degree of decomposition of organic matter. Other factors such as texture, altitude, relative freedom from drainage and differences in agricultural and manurial practice are doubtless also involved and contribute to the variations within groups. Considerable variability was observed in both C : S and N : S ratios of the soils collected from different regions (Table 2). It can be seen (Table 2) that while there is appreciable amount of variability within each region, mean C : S ratios of soil increased in the following order : Coastal Saline (56.8) < Lateritic (59.4) < Alluvial (73.4) < Hill (114.0) < Terai (164.0). The mean N : S ratios also increased in the soil following almost the same order as the mean C : S ratio : Lateritic (5 : 5) < Coastal Saline (5.6) < Alluvial (7.4) < Hill (14.5) < Terai (17.9). On a broader scale, the average N : S ratio for Hill and Terai regions was 16.2 whereas, that of plains was only 6.12. Organic matter of the acidic soils of semi temperate to temperate regions of Himalayan Hill and Terai are in a less decomposed state than in the plains. C : S, N : S ratio further indicate that the ratio of surface soils of all the twelve profiles were higher than those of the subsurface layers. This could result from difference in the nature of the organic matter itself. Similar observations were also reported by Virmani and Kanwar[5]. This explanation is partly confirmed by the studies of Williams and Steinbergs[13] who observed that organic matter varied in nature at various depths in soils. Although more detailed information on the nature and distribution of such

compounds in different soils and their relationships with soil properties is necessary to clarify this aspect, it is clear that carbon, nitrogen and sulphur are closely associated in the soil as organic matter (Fig. 1) and it seems possible that the proportions may be defined within moderately narrow limits by microbial decomposition.



Surface soil (0-15 cm.) Soils of all the three depths (0-45 cm.)

Fig. 1. Distribution of Organic Carbon, Total Nitrogen and Organic Sulphur among the Soil Zones
Organic C. × 1 ○—○ Total N. × 10 ●—● Organic S. × 100 ▲—▲

Acknowledgement

The first author is thankful to the Indian Council of Agricultural Research, New Delhi for awarding a Senior Fellowship to undertake this study.

References

1. J. S. Kanwar and S. Mohan, *Bull. Nat. Inst. Sci. India.*, 1964, **26**, 31.
2. J. S. Kanwar and P. N. Takkar, *J. Research*, 1964, **1**, 1.
3. S. Ahamed and K. K. Jha, *J. Indian Soc. Soil Sci.*, 1969, **17**, 197.
4. J. Venkateswarlu, B. V. Subbiah and R. V. Tamhane, *India J. Agric. Sci.*, 1969, **39**, 426.
5. S. M. Virmani and J. S. Kanwar, *J. Indian Soc. Soil Sci.*, 1971, **19**, 73.
6. C. Bhan and B. R. Tripathi, *J. Indian Soc. Soil Sci.*, 1973, **21**, 499.
7. V. Kumar and M. Singh, *J. Indian Soc. Soil Sci.*, 1974, **22**, 198.
8. A. K. Dutta, *Trop. Agr.*, 1962, **39**, 73.
9. A. K. Dutta, *Empire J. Expt. Agr.*, **30**, 257.
10. M. L. Jackson, *Soil Chemical Analysis*, 1968, 219.
11. J. M. Bremner, *J. Agr. Sci.*, 1960, **55**, 11.
12. C. E. Bardsley and J. D. Lancaster, Methods of Soil Analysis. Part-2. C. A. Black eds 1965, 1102.
13. C. M. Johnson and H. Nishita, *Anal. Chem.*, 1952, **24**, 736.
14. Partha Mukhopadhyay and Asit K. Mukhopadhyay, *J. Indian Soc. Soil Sci.*, 1980, **28** (in press).
15. C. H. Williams and A. Steinbergs, *Australian J. Agric. Res.*, 1959, **10**, 340.

J. Indian Chem. Soc.,
Vol. LVII, June 1980, pp. 620-623

Kinetics of Propionylation of Cellulose with 2,2-Dichloropropionic Acid

RAJESH K. JAIN, KRISHAN LAL and HARI L. BHATNAGAR

Chemistry Department, Kurukshetra University, Kurukshetra-132 119

Manuscript received 1 February 1980, accepted 19 May 1980

The reaction of cellulose with 2,2-dichloropropionic acid in chlorobenzene solvent in the presence of strong perchloric acid catalyst has been investigated as a function of time and temperature (30-60°). The reaction has been regarded to be taking place *via* the well-known $A_{AC}2$ mechanism. The products were characterized by elemental analysis and spectral techniques. The degree of substitution, p, in each prepared sample has been determined and assuming a second order reaction, the specific rate constants were calculated. With the help of the derived data, the enthalpy, the entropy and the free energy of activation have been obtained and interpreted.

A large number of cellulose derivatives has been synthesized[1a,2,3], including esters of inorganic and organic acids (apart from xanthate esters), ethers and graft co-polymers, although relatively few have achieved commercial importance. Organic esters are much more important at the present time. Malm and his co-workers[4] have prepared the whole series of cellulose esters from acetate to stearate by reaction of the free acid at 60-65° in the presence of impelling agent (chloroacetic anhydride) and a catalyst. In addition to this general method, there is another one which may be used, namely, the action of acid chlorides in the presence of a base, especially pyridine[5,6] or quinoline[7]. The cellulose acetates of varying degrees of substitution are prepared by first treating cellulose with acetic acid, then with acetic anhydride and a mineral acid catalyst. The fully acetylated product is subsequently reacted with water to achieve the desired degree of substitution. Cellulose propionate and cellulose butyrate, or, more commercially, acetate-propionate and acetate-butyrate mixtures are the only other commercially important cellulose esters. The mixed esters are generally more soluble and have better impact resistance than cellulose acetate. Esterification of cellulose with halogen-substituted acids provides an additional advantage as it has been observed that certain elements like nitrogen and halogens when incorporated into the matrix of cellulose impart flame resistance to it. In the following, a kinetic study of esterification of cellulose with 2,2-dichloropropionic acid has been described and the data analysed. So far no kinetic studies have been reported to date inspite of the potentialities of the reaction in flame proofing of cellulose[8]

Experimental

Reagents :

(i) *Cellulose :* The cellulose used was supplied by M/S. Dassel, West Germany. It was also dried over anhydrous calcium chloride under vacuum.

(ii) *Chlorobenzene :* The chemical used was supplied by M/S. Sarabhai M. Chemicals, India. It was dried over anhydrous calcium chloride and distilled. The distillate at 132° was collected for use.

(iii) *2,2-Dichloropropionic acid :* It was supplied by M/S. Koch Light Laboratories, Ltd., Colnbrook, Bucks, England and was used as such.

(iv) *Perchloric acid (60%) :* It was supplied by M/S. Riedel-De Haenag, Seelze, Hannover, Germany.

(v) *Sodium hydroxide, potassium hydroxide and silver nitrate :* All were of A.R. grade.

Propionylation of Cellulose : Propionylation of cellulose with 2,2-dichloropropionic acid for the definite periods of time at various temperatures was carried out in a three-necked flask immersed in an oil thermostat (constancy $\pm 0.5°$) and fitted with a water condenser having a guard tube at its open end and a mercury sealed stirrer. Each time, 1.62 g of dry cellulose powder was allowed to get swollen in 10 ml of chlorobenzene for one hour period at the temperature of the experiment in a flask before the start of the reaction. This was done to increase the reactivity of cellulose. 4.2896 g of 2,2-dichloropropionic acid was added in 36.4 ml of chlorobenzene and allowed to attain the temperature of the experiment, then transferred to the flask containing cellulose mixed with perchloric acid (about 8% on the weight of cellulose). Perchloric acid catalyst was used as it was reported to have greater catalytic activity than the phosphoric acid or hydroiodic acid[9]. The reaction mixture was continuously stirred and refluxed for a given period at a given temperature. The medium was heterogeneous throughout the reaction period. The product was filtered through G-4 sintered glass funnel, washed thoroughly with distilled water, dried first in air

and then over P_2O_5 under vacuum. The samples of dichloropropionylated cellulose were stored in vacuum desiccator containing P_2O_5 as they were found to be highly hygroscopic.

The chlorine in the samples was estimated by the Carius method. From the % of chlorine in the sample (x), the degree of substitution (p) of the various samples was calculated using the equation[1b],

$$p = \frac{162x}{100 \times 142.98 - 124.98x} \quad \ldots \quad (1)$$

where 162 and 142.98 are the molecular weights of anhydroglucose unit and 2,2-dichloropropionic acid respectively and 124.98 is the net increase in the molecular weight of cellulose resulting from the introduction of one substituent (CH_3CCl_2CO-) in one anhydroglucose unit.

Spectral Studies :

Infrared spectra of the samples in KBr pellets were obtained using Beckmann spectrophotometer, Model IR-20 (USA). Each sample (0.5-1.0 mg) was intimately mixed with 100 mg of dry powdered potassium bromide and its infrared spectra recorded.

The NMR spectra of acetone soluble part of the treated cellulose sample in DMSO-d_6 solution was recorded using Perkin-Elmer R-32, 90 MHz Spectrophotometer (U.K.). The chemical shifts were expressed in ppm downfield from TMS.

Theoretical considerations :

The reaction of cellulose with 2,2-dichloropropionic acid was throughout heterogeneous in nature. Under such conditions, all the hydroxyl groups in the anhydroglucose unit could be assumed to have the same reactivity[10]. This is an over simplification and probably only the primary $-OH$ groups have the same reactivity irrespective of the chain length. Now, if the concept of equal reactivity of all the functional groups ($-OH$) irrespective of the size of polymer molecule[11] was assumed, then for a second order reaction, the rate equation can be formulated as,

$$-\frac{d}{dt}[OH] = k_r[COOH \text{ in I}][OH \text{ in II}], \quad \ldots \quad (2)$$

$$\text{where } I = ClO_4^{\ominus}\left[CH_3CCl_2-\overset{\overset{\oplus}{O}H}{\overset{\|}{C}}-OH\right],$$

$$\text{and } \quad II = \begin{matrix} HO \\ HO \end{matrix}\!\!>\!Cell-\ddot{O}-H.$$

In order to eliminate the difficulties of writing a separate equation for the reaction for each hydroxyl group of cellulose with 2,2-dichloropropionic acid, it was assumed that rate constant k_r was the same for all hydroxyl groups and did not change as the average molecular weight of cellulose increased.

Anhydroglucose units in the form of cellulose and 2,2-dichloropropionic acid were taken in the molar ratio 1 : 3 so that the initial molar concentration of the $-OH$ groups of cellulose was the same as that of $-COOH$ groups of 2,2-dichloropropionic acid (0.75*M*). Thus, if 'C_0' was the initial concentration of $-OH$ groups of cellulose and 'C' was the concentration of the $-OH$ groups at any time, t, the two may be related by the expression,

$$C = (1 - p')C_0, \quad \ldots \quad (3)$$

where, p', represented the extent of the reaction or the fraction of the hydroxyl groups initially present that had undergone reaction in a given time 't'.

Let, p, the degree of substitution, represent the average number of molecules of 2, 2-dichloropropionic acid combined with each anhydroglucose unit having molecular formula $C_6H_7O_2(OH)_3$. Under these considerations, equation (2) may be rewritten as

$$k_r = \frac{p}{C_0(3-p)t}, \quad \ldots \quad (4)$$

Thus, a plot of $p/(3-p)$ versus 't' would give a straight line passing through the origin and having slope equal to $C_0.k_r$. The specific reaction rate constant k_r can be calculated using the experimental value of the slope.

Results and Discussion

An important evidence for the reaction mechanism is to identify the products formed. All the solid products formed were identified by elemental analysis, infrared and NMR techniques. For spectral studies, it was found desirable to study the IR and NMR spectra of single components separately and compare the same with the spectra obtained on systems consisting of combination of the compounds.

The Infrared spectra of the treated sample exhibited strong carbonyl (1740 cm^{-1}) absorption bands due to stretching vibration of C=O bond in the ester group. A relative decrease in the intensity of hydroxyl band at 3600 cm^{-1} was also observed. The presence of the band at 1110 cm^{-1} in the prepared samples was believed to be associated with the pyranole ring motion in the amorphous cellulose. The acetone soluble part of the propionylated products showed strong IR absorption peak at about 650 cm^{-1}. The spectra indicated the presence of chloropropionylated cellulose as well as amorphous cellulose. The various frequencies bands of the reactants and products are given in Table 1.

TABLE 1—COMPARISON OF INFRARED SPECTRAL BANDS OF CELLULOSE, 2,2-DICHLOROPROPIONIC ACID AND DICHLOROPROPIONYLATED CELLULOSE

(IR bands in cm^{-1})

Cellulose	2,2 Dichloro-propionic Acid	Dichloropropionylated Cellulose	Band characterisation (assignment)
3300-3600	—	3300-3600	O–H stretching
2900	—	2900	C–H stretching
—	1740	1740	C=O stretching in ester group
1640	—	1640	H–O–H stretching
1440	1440	1440	CH_2 bending
1380, 1320	—	1380, 1320	O–H bending
1110	1110	1110	C–OH stretching
1050	—	1050	Cellulose
900	—	900	Amorphous cellulose

The formation of cellulose 2, 2-dichloropropionate has been further established by comparing its 90 MHz NMR spectrum (Fig. 1) with that of commercial cellulose acetate. The typical $-CH_3$ proton signal which shows up at δ 2.08 in the case of commercial cellulose acetate showed a downfield shift in this product, appearing at δ 2.35 which can be attributed to the deshielding effect of the chlorine atoms on the neighbouring carbon atom. In addition. the signal in the range of δ 10.8-δ 11.8 (1H, $-COOH$) was also found to be absent in the product.

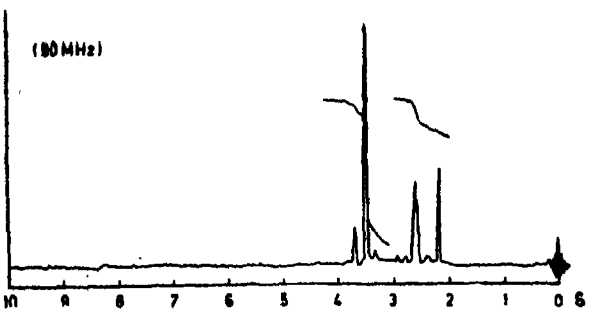


Fig. 1. Nuclear Magnetic Resonance Spectra of 2, 2-Dichloropropionylated Cellulose.

The present system follows a mathematical discipline of second order, which rules out the operation of unimolecular $A_{AC}1$ and $A_{AL}1$ mechanisms[12,13]. As the reaction has been carried out under the conditions that are very similar to a typical acid-catalyzed esterification, it can be regarded to be taking place *via* the well known $A_{AC}2$ mechanism. It is well known that the esterifications taking place by $A_{AC}2$ mechanism are reversible, it becomes necessary to remove water from the medium if this is to be used as a preparative method for the formation of the ester. During the present investigations, nitrogen gas was passed into the reaction mixture in order to remove the water formed.

The percentage of chlorine in the products prepared after different intervals of time at various temperatures were estimated gravimetrically and the degree of substitution in each treated sample was calculated using equation (1) and has been listed in Table 2.

TABLE 2—DEGREE OF SUBSTITUTION OF THE TREATED CELLULOSE SAMPLES AS A FUNCTION OF TIME

Time in hours	%Cl	%Combined CH_3CCl_2COOH	Degree of Substitution (p)	$\frac{p}{(3-p)}$
		Temperature 30°C		
0.5	0.1571	0.3164	0.0036	0.0012
1.0	0.2724	0.5485	0.0062	0.0021
1.5	0.4131	0.8319	0.0095	0.0032
2.0	0.5569	1.1214	0.0128	0.0043
2.5	0.6787	1.3667	0.0157	0.0053
3.0	0.8085	1.6281	0.0187	0.0063
3.5	0.9106	1.8335	0.0211	0.0071
4.0	1.0520	2.1185	0.0245	0.0082
		Temperature 40°C		
0.5	0.1702	0.3427	0.0039	0.0013
1.0	0.3343	0.6732	0.0077	0.0026
1.5	0.4852	0.9771	0.0112	0.0037
2.0	0.6508	1.3096	0.0150	0.0050
2.5	0.8156	1.6425	0.0189	0.0063
3.0	1.0032	2.0202	0.0233	0.0078
3.5	1.1563	2.3285	0.0269	0.0091
4.0	1.3148	2.6467	0.0307	0.0103
		Temperature 50°C		
0.5	0.2126	0.4281	0.0049	0.0017
1.0	0.3928	0.7910	0.0090	0.0030
1.5	0.5704	1.1487	0.0131	0.0044
2.0	0.7551	1.5206	0.0175	0.0059
2.5	0.9607	1.9346	0.0223	0.0075
3.0	1.1467	2.3092	0.0267	0.0090
3.5	1.3252	2.6687	0.0309	0.0104
4.0	1.5104	3.0416	0.0354	0.0119
		Temperature 60°C		
0.5	0.2881	0.5802	0.0066	0.0022
1.0	0.4601	0.9265	0.0106	0.0035
1.5	0.6864	1.3822	0.0158	0.0053
2.0	0.9059	1.8243	0.0210	0.0071
2.5	1.0742	2.1632	0.0250	0.0084
3.0	1.3320	2.6824	0.0311	0.0105
3.5	1.5758	3.1733	0.0370	0.0125
4.0	1.6811	3.3854	0.0395	0.0134

Values of k_r as calculated by least squares method at different temperatures are: 30°C, 9.3×10^{-7}; 40°C, 12.1×10^{-7}; 50°C, 13.7×10^{-7}; and 60°C, 15.4×10^{-7} l $mol^{-1}s^{-1}$.

The plots of $p/(3-p)$ versus time for the various systems are shown in Fig. 2. These plots were found to be linear. The average value of the specific reaction rate k_r were determined by the method of least squares.

In order to calculate the energy of activation for this process, different values of ln k_r obtained at the various temperatures were plotted against. The method of least squares was used to evaluate the experimental energy of activation and the frequency factor A. The value of ΔE_{exp} and A were found to be 13.7 kJ mol^{-1} and 4.5×10^{8} l $mol^{-1}s^{-1}$ respectively.

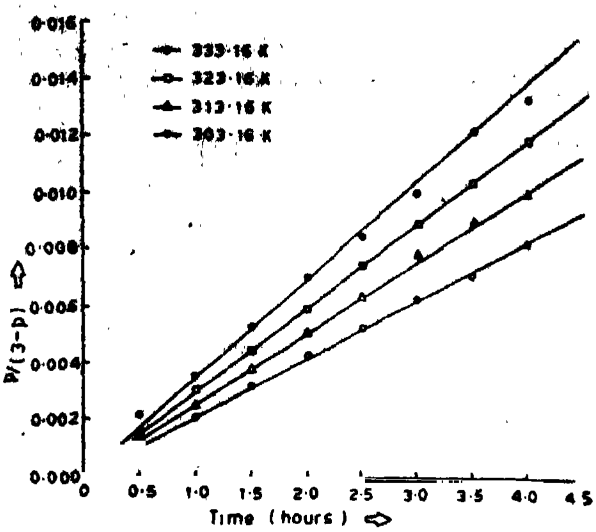


Fig. 2. Effect of Temperature on the Reaction of Cellulose with 2, 2-Dichloropropionic acid

The value of entropy of activation for the reaction was calculated from the equation $A = (ekT/h)\, e^{\Delta S^*/R}$. At 318.16 K, the average temperature of the experiment, the value of ΔS^* was found to be -183.8 J deg^{-1} mol^{-1}.

The value of ΔH^* and ΔG^* were found to be 11.1 kJ mol^{-1} and 69.6 kJ mol^{-1} respectively.

The qualitative explanation of the negative entropy of activation can be given as follows. The formation of an activated complex from reactant molecules is accompanied by the conversion of translational-like and rotational-like degrees of freedom of the reactants to vibrational degrees of freedom of transition state species. The more widely spaced energy level for the latter type of molecular motion imply smaller entropy and thus the negative value of ΔS^*. A decrease in the value of ΔS^* (-183.8 J deg^{-1} mol^{-1}) in the system cellulose—2, 2-dichloropropionic acid conforms to the above explanation.

Acknowledgement

Authors are grateful to the United States Department of Agriculture, Eastern Agriculture Research Service, for supporting the research under the grant No. FG-In-524, Project No. UR-A7-(20)-219 of research fellowship to R. K. J. Thanks are also due to Dr. I. S. Gur and Dr. R. P. Kapoor of this Department for useful suggestions in the present work.

References

1. E. Ott, H. M. Spurlin and M. W. Grafflin, Eds., "Cellulose and Cellulose Derivatives", 2nd Ed., Part II, Wiley-Interscience, New York 1954 ; (a) Chapter IX, (b) p. 1492.
2. E. M. Fettes, Ed., "Chemical Reactions of Polymers", Wiley-Interscience, New York, 1964 ; (a) K. Ward, Jr. and A. J. Morak, Chapter V ; (b) M. G. Gaylord and F. S. Ang, Chapter X, (c) W. A. Reeves and J. D. Guthrie, Chapter XVI, (d) R. E. Whitfield and W. L. Wasley, Chapter VI.
3. B. G. Ranby and S. A. Rydholm, "Polymer Process", C. E. Schildknecht, Ed., Wiley-Interscience, New York, 1956, Chapter IX.
4. H. T. Clarke and C. J. Malm, *U. S. Patent*, 1,880,808 (to Eastman Kodak Co.), Jan. 8, 1929 ; *C. A.*, 1929, **23**, 1267.
5. M Hagedorn and P. Möller, *Cellulosechemie*, 1931, **12**, 29 ; *C. A.*, 1931, **25**, 5982.
6. C. J. Malm, J. W. Mench, D. L. Kendall and G. D. Hiatt, *Ind. Eng. Chem.*, 1951, **43**, 684.
7. H. Pringsheim, E. Lorand and K. Ward, Jr., *Cellulosechemie*, 1932, **13**, 119 ; *C. A.*, 1932, **26**, 6123.
8. R. K. Jain, S. Bhatnagar, K. Lal and H. L. Bhatnagar, *Indian J. Chem.*, (in Press).
9. V. M Vasil'ev and V. I. Sharkov (USSR), *Khim. Tekhnol. Proizvod. Tsellyal*, 1971, 53 (Russ) ; *C. A.*, 1973, **78**, 136115b.
10. N. K. Pytakina, Yu. V. Moiseev and G. E. Zaikov, *Vysokomol. Soedin*, Ser. A, 1975, **17(7)**, 1498 ; *C. A*, 1975, **83**, 149849e.
11. P. J. Flory, "Principle of Polymer Chemistry", Cornell University Press, New York, 1953.
12. C. K. Ingold, "Structure and Mechanism in Organic Chemistry", Bell, London, 1953, Chapter XIV.
13. S. D. Hamann, D. H. Soloman and J. D. Swift, *J. Macromol. Sci. Chem.*, 1968, **A2**, 153.
14. W. L. Barnett, *J. Soc. Chem. Ind.* (London), 1921, **40**, 253T ; *C. A.*, 1922, **16**, 341.

J. Indian Chem. Soc.,
Vol. LVII, June 1980, pp. 624-628

Medium Dependence of Acid-Catalyzed Formamide Hydrolysis

I. M. SIDAHMED, S. M. SALEM and F. M. ABDEL HALIM

Chemistry Department, Faculty of Science, Alexandria University, Moharram Bey, Alexandria, Egypt.

Manuscript received 27 October 1979, accepted 9 April 1980

The acid hydrolysis of formamide was carried out in aqueous-, methanol, ethanol, *n*-propanol, isopropanol, tert-butanol and ethylene glycol.

The rate of the reaction was found to increase in aqueous-, methanol and ethylene glycol and to decrease continuously in aqueous isopropanol while minima were observed in the other solvents. This behaviour was interpreted on the basis of the solvent structure and the role of water in the mechanism of the reaction.

FROM the theoretical point of view, it is well known that, the solvation process gives the system a state of stability as a result of the energy lost in the electrostatic work done due to this process. It is also a known fact that equilibria will shift towards more polar products in more polar solvents.

These rational points of view made Hughes and Ingold[1] to assume that the energy change will dominate the rate change, where the more polar solvent will enhance or retard the reaction depending on whether the transition state is more or less polar than the initial state.

In the literature, there are data which support[2] this postulate ; also there are other data which do not[3] as found in the present investigation.

It is thus pertinent to enlarge the scope of the traditional treatment of the medium effect, specially the electrostatic properties of the medium, and invoke other factors which seem to give reasonable interpretation of these anomalous data.

Experimental

Purification of solvents and Formamide : The solvents and formamide which have been used in this work were of the best grade available from B.D.H. ; further purification for each solvent and formamide were carried out as reported[4]. Solvent mixtures were usually made up by weight, and the ratio of the formamide : hydrochloric acid was 1 : 1 where the concentration of each reactant was 0.1 *M*.

The kinetic technique (ion exchange) has been described[5], and second order kinetic was observed for at least 80% reaction. The reaction was thermostated at 25°±0.02°. Complete hydrolysis was assured by the coincidence of the theoretical and the experimental values.

Results and Discussion

The rate of the acid hydrolysis of formamide was measured in methanol-, ethanol-, *n*-propanol, isopropanol, tert-butanol, and ethylene glycol-water mixtures in the range from 0.0% to almost 90% by weight organic solvent. The hydrolysis was found to follow a second order kinetic rate equation. A typical example of the acid hydrolysis of formamide in ethanol-water mixtures is shown in Fig. 1. From such plots, extrapolated values for the specific rate constant were obtained and assembled in Table 1, and represented graphically in Fig. 2.

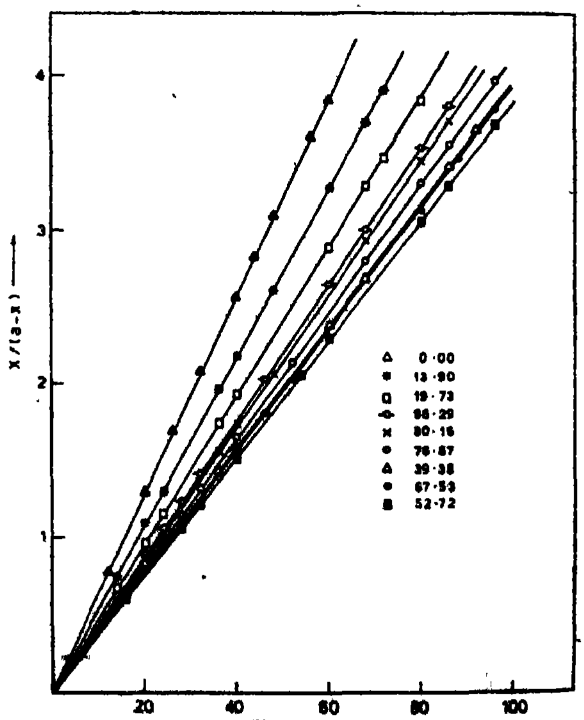


Fig. 1. Second order plots at 25° in ethanol-water mixtures.

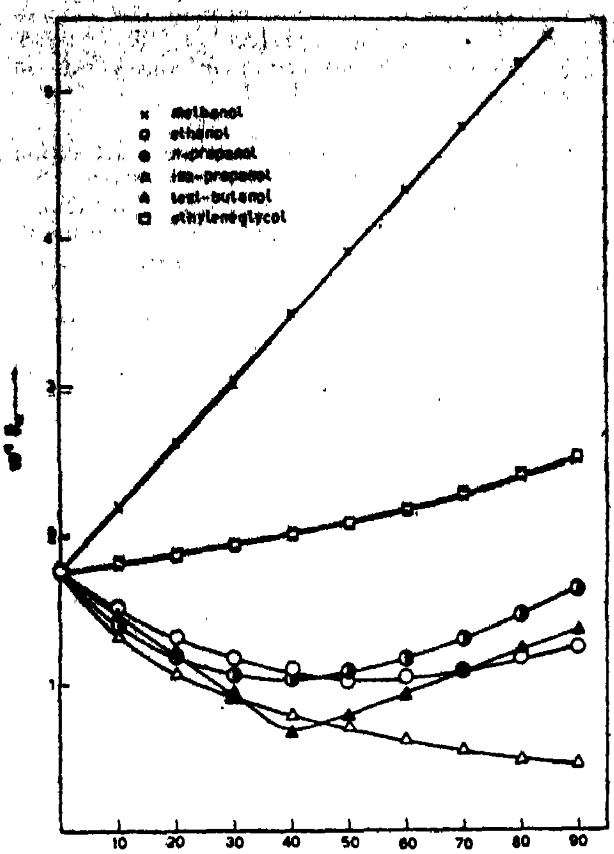


Fig. 2. Variation of k_2 with wt% alcohol.

TABLE 1—RATE CONSTANTS (In l-mole[-1] sec[-1]) FOR THE ACID HYDROLYSIS OF FORMAMIDE IN PRESENCE OF ALCOHOL-WATER MIXTURES AT 25°C

Solvent wt%	$10^4 k_2$ methanol	ethanol	n-propanol	isopropanol	t-butanol	ethylene glycol
0	1.765	1.765	1.765	1.765	1.765	1.765
5	1.975	1.638	1.580	1.520	1.628	1.790
10	2.185	1.532	1.415	1.330	1.490	1.815
15	2.400	1.414	1.280	1.190	1.350	1.848
20	2.620	1.321	1.160	1.070	1.211	1.878
25	2.880	1.242	1.105	0.990	1.070	1.905
30	3.042	1.174	1.055	0.917	0.929	1.938
35	3.255	1.122	1.026	0.848	0.788	1.972
40	3.475	1.087	1.026	0.790	0.685	2.007
45	3.690	1.060	1.035	0.742	0.700	2.043
50	3.900	1.044	1.055	0.700	0.778	2.082
55	4.110	1.045	1.092	0.655	0.827	2.125
60	4.330	1.055	1.160	0.615	0.921	2.172
65	4.550	1.074	1.23[illegible]	0.575	0.995	2.225
70	4.760	1.102	1.306	0.538	1.068	2.283
75	4.985	1.136	1.388	0.510	1.142	2.343
80	5.200	1.176	1.463	0.480	1.215	2.400
85	5.410	1.218	1.545	0.460	1.290	2.465
90	5.640	1.262	1.640	0.440	1.362	2.525

The effect of the dielectric constant : According to the Hughes and Ingold theory[1], the rate of the reaction between an ion and a dipolar molecule, must increase as the polarity of the solvent decreases due to the dispersal of the charge on the activated complex. Aqueous, methanol and ethylene-glycol show perfect agreement with such theory, but the reaction in the other solvents shows anomalous results as shown in Fig. 3.

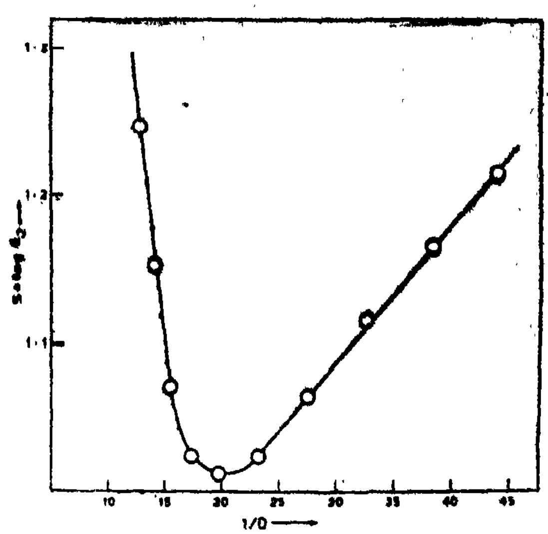


Fig. 3. Influence of dielectric constant on k_2 in n-propanol-water mixtures.

To interpret these anomalous data we have to take into consideration two factors : (a) the role of water in the mechanism of the reaction, and (b) the change in the structure of water in the mixed solvent which may take place as the composition changes.

The role of water in the mechanism : Bunnett[6], developed an approach which was used as a criterion of mechanism based on detailed analysis of results for many reactions. The reactions are classified into three groups : (a) those in which water does not participate in the rate determining step, (b) those in which water acts as a nucleophile in the rate determining step, and (c) those in which water acts as a proton transfer agent in the rate determining step.

Alternatively the linear free energy relationship proposed by Bunnett and Olsen[7],

$$\log k_2 + H_0 = \phi(H_0 + \log C_{H^+}) + \text{constant}$$

has been applied and presented graphically (Fig. 4), the values of H_0, have been used as reported in literature[8].

The range of the slope ϕ for different modes of involvement of water in the rate determining step were reported as, $-0.34 < \phi < 0$ for water being not involved, $0.18 < \phi < 0.47$ for water acting as a

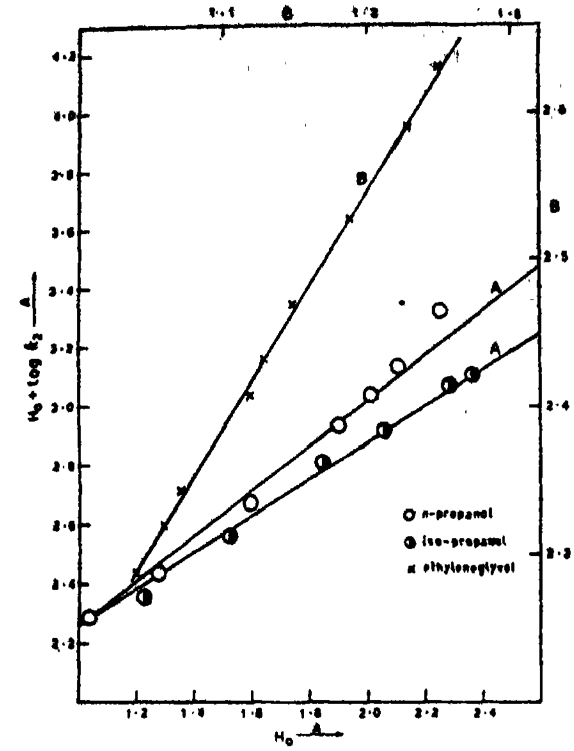


Fig. 4. Test of the linear free energy relationship for the hydrolysis of formamide in organic solvent-water mixtures.

nucleophile and ø>0.47 for water acting as a proton transfer agent. The latter case is in agreement with our present investigation since the values of ø are found to be 0.74, 0.71 and 1.6 for aqueous-, *n*-propanol, isopropanol and ethylene glycol respectively, and accordingly the existence of free water molecules in systems representing the different types of behaviour is necessary to enhance the reaction rate.

The behaviour of water in the mixed solvent : Several arguments have been put forward in order to interpret the changes in the proton availability with medium composition[9-13]. But experimentally it has been found that the nature and properties of the organic component may affect such proton availability. On the other hand, the solute may bring about a marked change in the state of the solvent components, since it may cause a marked increase in the activity in one of the solvent components and a marked decrease in that of the other[13].

Experimental evidence on the behaviour of binary mixtures of simple aliphatic alcohols and water has indicated that dilute solutions of the higher alcohol homologs cause the building up of the structure of water to be enhanced[14-16]. The hydrocarbon groups in the alcohols provide sites for the build-up of structure around the alcohol molecule ; the peculiar structural features of aqueous alcohol solutions produce remarkable effects on the reaction kinetics[17].

In aqueous organic solvent mixtures, activation energies, activation volumes, heat of solution[18-21], internal pressure[22], conductance and transference number[23] often show maxima and/or minima as the composition of the solvent changes. Accordingly we may add that the minima which have been observed in the present work, particularly in aqueous-, ethanol, *n*-propanol, and tert-butanol are due to the enhancement of the structure of water at the region of the high dielectric constant.

In case of methanol-water mixtures, the build-up of structure of water around the alcohol molecule does not occur since methanol shows about 1 : 1 association with water[24] that does not change very much even at higher alcohol concentrations where alcohol-alcohol interaction becomes important. Moreover, the interaction between the proton and the water molecule in the mixture should be stronger than in pure water, since the inductive effect of the methyl group makes the methanol molecule more basic and less acidic than the water molecule[25] where the negative charge on the oxygen atom is greater and the positive charge on the hydroxylic hydrogen atom is less. Cooperative hydrogen bonding transmits these characteristics also to the water molecules in the mixture. Therefore, the increasing affinity of water to the proton and the nonassociation of water molecules in methanol lead to the enhancement of the hydrolysis continuously by the successive addition of methanol.

It has been postulated that[8] the glycol and water molecules slightly effect mutually their electron envelopes and thus no association is forthcoming. On the other hand, ethylene-glycol possess a greater acidity[26] than the other alcohols ; this possibly arises from its capacity to form inter- and intra-molecular hydrogen bonds which increases the "B Strain" in the protonated molecule, and leads to a decrease in the electron-releasing power of the $-CH_2$ groups, resulting in a lower electron- density on both the oxygen atoms, and thus facilitating the removal of the proton ; in this case the hydronium ion will predominate.

It has been expected that, the effect of ethylene glycol should be more pronounced than methyl alcohol since it is well known that glycol is more acidic than methanol. On electrostatic grounds[27], it was postulated that the solvation by water is greater in water-methanol rather than in water glycol.

If we can treat the polar formamide molecule as an ion, where charge separation occurs when it

reaches the activated state, then it will be preferentially solvated in aqueous glycol by the highly polar component, water, but to a lesser extent than that in methanol-water mixture.

The acid hydrolysis of formamide in aqueous isopropanol has a peculiar behaviour as compared to the hydrolysis in the other aqueous alcohols where a continuous decrease in the rate was observed even at high alcohol concentrations.

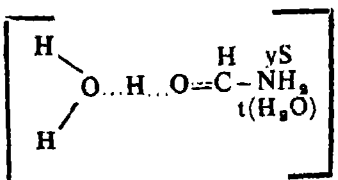
At the instant when the build-up structure of water will be gradually dispersed as the proportion of the alcohol is increased, the following equilibrium[11] will be established,

$$(H_2O)_nH^+ + ROH \rightleftharpoons ROH_2^+ + nH_2O.$$

Due to the high basicity of isopropanol[8] the equilibrium will be shifted almost completely to the right and the protonated species are supposed to change from $(H_2O)_nH^+$ to water solvated ROH_2^+ ions.

A mechanism was proposed[26] for the acid catalysed hydrolysis of formamide which may be in agreement with the present investigation.

$$\text{Amide} \ldots mH_2O + H_3O^+ \ldots nH_2O + yS + t(H_2O) \underset{k_2}{\overset{k_1}{\rightleftharpoons}}$$



Fastpre-equilibrium

$+ (m+n)H_2O$

T

$$T \xrightarrow[\text{slow}]{k_3} \text{products} + yS + t(H_2O)$$

Considering k_3 being small in comparison with k_2, thus,

$$\text{rate} = \frac{k_1 k_3}{k_2} \frac{[\text{Amide}][H_3O^+][S]^y}{[H_2O]^x}$$

where $x = (m+n) - t$, and it represents the difference in solvation between the ground and the activated states.

In case of methanol-water and ethylene glycol-water mixtures the fraction $[H_3O^+]/[H_2O]^x$ should increase by increasing the concentration of the organic solvent component, so the rate will increase continuously, while in the case of ethanol, *n*-propanol, and tert-butanol-water mixtures the activity of the hydronium ion should pass through a minimum due to the build-up of the structure of water.

The increase in concentration of isopropanol will result in a decrease of the activity of the hydronium ion due to its high basicity compared to water. The effect of this decrease on the reaction rate is found to be more pronounced than the expected increase in rate as a result of the increase in the solvent concentration. The final result would be a continuous decrease in the rate with successive addition of isopropanol.

References

1. C. K. INGOLD, "Structure and Mechanism in Organic Chemistry". Cornell University Press, 1953, p. 345.
2. HUSSEIN SADEK and F. Y. KHALIL, *Suomen Kemistilehti B*, 1967, **40**, 59.
3. HUSSEIN SADEK and F. Y. KHALIL and M. T. HANNA, *Z. Phys. Chemie, NeueFolge*, 1970, **73**, 77.
4. A. I. VOGEL, "A Text-Book of Practical Organic Chemistry", 1971, 3rd Ed.
5. M. M. ELSEMONGY, M. S. ABU ELAMAYEM and M. MOUSSA, *Z. Phys. Chemie. NeueFolge*, 1975, **95**, 215.
6. J. F. BUNNETT, *J. Amer. Chem. Soc.*, 1961, **83**, 4956, 4968, 4973, 4978.
7. C. H. ROCHESTER, "Acidity Functions", Academic Press, London and New York, 1970, p. 117.
8. A. R. TOURKY, A. A. ABDEL-HAMID and I. Z. SLIM, *Z. Phys. Chemie, Leipzig.*, 1973, **250**, 49, 60.
9. E. A. BRAUDE, *J. Chem. Soc.*, 1948, 1971 ; E. A. BRAUDE, and E. S. STERN, *J. Chem. Soc.*, 1948, 1976.
10. E. WICKE, M. EIGEN and H. ACKERMAN, *Z. Phys. Chemie.*, 1954, 340 ; K. N. BASCOMBE and R. P. BELL, *Discuss. Farad. Soc.*, 1957, **24**, 158.
11. C. F. WELLS, *Discuss Farad. Soc.*, 1965, **39**, 132 ; C. F. WELLS, *Trans. Farad. Soc.*, 1965, **61**, 2194 ; *Trans. Farad. Soc.*, 1966, **62**, 2815.
12. G. SCATCHARD, *J. Amer. Chem. Soc.*, 1925, **47**, 641, 2098 ; J. A. V. BUTLER and G. M. ROBERTSON, *Proc. Roy. Soc.*, 1929, **A125**, 694 ; H. S. FRANK, and M. W. EVANS, *J. Chem. Phys.*, 1945, **13**, 507.
13. E. GRUNWALD, G. BAUGHMAN and G. KOHNSTAM, *J. Amer. Chem. Soc.*, 1960, **82**, 5801 ; W. J. MILLER and E. GRUNWALD, *J. Phys. Chem.*, 1964, **68**, 1285.
14. F. FRANKS and D. IVES, *Quart. Rev.*, 1966, **20**, 1.
15. G. WADA and S. UMEDA, *Bull. Chem. Soc. Japan*, 1962, **35**, 646.
16. J. A. V. BUTLER, *Trans. Farad. Soc.*, 1935, **32**, 229.
17. E. M. ARNETT, P. M. DUGGLEBY and J. J. BURKE, *J. Amer. Chem. Soc.*, 1963, **85**, 1351.
18. A. H. FAINBERG and S. WINSTEIN, *J. Amer. Chem. Soc.*, 1956, **78**, 2770 ; S. WINSTEIN and A. H. FAINBERG, *J. Amer. Chem. Soc.*, 1957, **79**, 5937.
19. J. B. HYNE, R. WILLS and R. E. WONKKA, *J. Amer. Chem. Soc.*, 1962, **84**, 2914.
20. E. M. ARNETT, W. G. BENTRUDE, J. J. BURKE and P. M. DUGGLEBY, *J. Amer. Chem. Soc.*, 1965, **87**, 1541 ; E. M. ARNETT, W. G. BENTRUDE and P. M. DUGGLEBY, *J. Amer. Chem. Soc.*, 1965, **87**, 2084.
21. J. B. HYNE, H. S. GOLINKIN and W. G. LAIDLAW, *J. Amer. Chem. Soc.*, 1966, **88**, 2104 ; H. S. GOLINKIN, I. LEE and J. B. HYNE, *J. Amer. Chem. Soc.*, 1967, **89**, 1307 ; C. S. DAVIS and J. B. HYNE, *Can. J. Chem.*, 1972, **50**, 2270.

22. D. D. MACDONALD, J. B. HYNE and F. L. SWINTON, *J. Amer. Chem. Soc.*, "Communications to the Editor", 1970, 92, 6855.

23. T. L. BROADWATER and R. L. KAY, *J. Phys. Chem.*, 1970, 74, 3802.

24. C. H. SPINK and J. C. WYCKOFF, *J. Phys. Chem.*, 1972, 76, 11, 1660.

25. D. FEAKINS and P. WATSON, *J. Chem. Soc.*, 1963, 4734.

26. C. H. KALIDAS and S. R. PALIT, *J. Chem. Soc.*, 1961, 3998.

27. E. S. AMIS, 'Solvent Effects on Reaction Rates and Mechanism", Academic Press, 1966, p. 18.

28. I. M. SIDAHMED, A. E. EL-KHOLY, Y. M. ABU ELAMAYEM and S. EL-SHAZLY, Revue Roumaine De Chimie, 1979, accepted for publication.

J. Indian Chem. Soc.,
Vol. LVII, June 1980, pp. 629-632

Thermodynamic and Spectroscopic Study of 6-Methyluracil

D. FERRO°, L. BENCIVENNI, R. TEGHIL and M. PELINO

Centro per la Termodinamica Chimica alle Alte Temperature C.N.R.
C/o Istituto di Chimica Fisica—Università di Roma, Italy

Manuscript received 19 February 1980, accepted 9 April 1980

The vapour pressure of 6-methyluracil was measured in the temperature range 426-503K by the torsion effusion technique and pressure-temperature equation : lgP(kPa) = 12.09 ± 0.07 − (6652 ± 34)/T was determined. The sublimation enthalpy ΔH°_{298} = 131 ± 7 kJ/mol was derived as mean of the results obtained by the second and third law treatment of the experimental vapour pressure data. The spectroscopic measurements of an infrared investigation on gaseous 6-methyluracil were employed in the thermodynamic functions calculations.

THE biological importance of uracil and its derivatives has prompted to several spectroscopic[1-3] and mass spectrometric[4] investigations. As a part of our ongoing research program for the thermodynamic study of uracil[5] and other pyrimidine bases, the vapour pressure and the thermodynamic functions of 6-methyluracil have been determined. The vapour pressure measurements of this compound were carried out by using the torsion effusion method. The discussion and the assignment of the infrared gas phase spectrum of 6-methyluracil are also reported.

Experimental

The sample was kindly supplied by the Ungarian Academy of Sciences and purified by recrystallizing from water and then it was sublimated under vacuum. A check of its purity was made by measuring the melting point of the sample 594 ± 1K (593 ± 1K).[6]

(A) Vapour Pressure measurements :

The basis of the method is well known[7,8] when the sample, contained in a graphite cell and suspended by means of a tungsten wire in the isothermal region of the furnace, is heated under vacuum, the vapour pressure is derived by the measure of the torsion angle α of the cell through the relation :

$$P = 2K\alpha/(a_1 l_1 f_1 + a_2 l_2 f_2)$$

where K is the constant of the torsion wire (30 in diameter and 35 cm in length), a_1 and a_2 are the areas of the effusion holes, l_1 and l_2 are the respective distances from the rotation axis and f_1 and f_2 the corresponding geometrical correction factors. In this study the correction factors are derived from the equation[9] $1/f = 0.0147(R/r)^2 + 0.3490(R/r) + 0.9982$ where r and R are the radius and the thickness of the effusion hole respectively. The temperature of the cell was measured by a calibrated chromel-alumel thermocouple inserted in a second cell below the torsion crucible. In order to test the thermodynamic equilibrium existing within the used cell and the reliability of the temperature measurements, the sulphur vapour pressure was determined in the temperature range 390-510 K and the obtained data were compared with the selected ones reported by Hultgreen[10].

The vapour pressure of 6-methyluracil determined in two runs over the temperature range 426-503 K are reported in Table 1 and plotted in Fig. 1. The straight line lgP against 1/T obtained by least square treatment of the experimental data is given

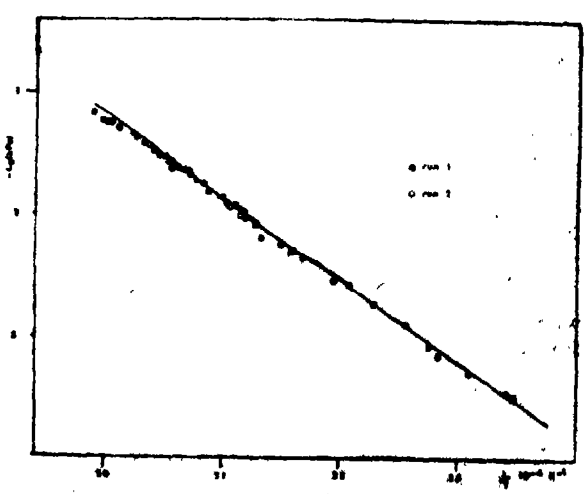


Fig. 1. Vapour pressure experimental values of 6-methyluracil.

TABLE 1—VAPOUR PRESSURE DETERMINED BY TORSION-EFFUSION METHOD

T (k)	number of points	α^a (degree)	P (kPa)	$-\Delta[(G^\circ_T - H^\circ_{298})/T]$ (J/K mol)	ΔH°_{298} (kJ/mol)
Run 1					
426	1	2	3.53 10^{-4}	200.7	180.0
433	1	3	5.29 ,,	200.7	180.6
439	1	5	8.88 ,,	200.6	180.6
443	1	7	1.26 10^{-3}	200.5	180.4
455	1	17	3.00 ,,	200.4	180.6
461	1	26	4.59 ,,	200.4	180.7
469	2	33	6.71 ,,	200.3	181.0
470	6	49	8.65 ,,	200.3	180.7
472	5	60	1.06 10^{-2}	200.3	180.4
473	3	64	1.13 ,,	200.3	180.5
474	2	69	1.58 ,,	200.3	180.5
475	3	73	1.29 ,,	200.3	180.5
476	2	80	1.41 ,,	200.2	180.4
479	3	90	1.59 ,,	200.2	180.7
480	3	105	1.85 ,,	200.2	180.4
482	1	125	1.98 ,,	200.2	180.2
483	3	130	2.30 ,,	200.2	180.3
484	2	135	2.38 ,,	200.2	180.5
486	2	150	2.80 ,,	200.1	181.1
488	2	170	3.00 ,,	200.1	180.6
489	3	178	3.06 ,,	200.1	180.8
491	3	209	3.69 ,,	200.1	180.5
492	3	216	3.81 ,,	200.1	180.6
493	3	250	4.41 ,,	200.1	180.8
495	2	273	4.91 ,,	200.0	180.4
496	2	300	5.30 ,,	200.0	180.8
499	6	330	5.82 ,,	200.0	180.7
501	1	345	6.09 ,,	200.0	181.0
503	1	404	7.13 ,,	200.0	180.9
				Average	180.6 ± 0.2^b
Run 2					
427	2	2	3.53 10^{-4}	200.7	180.3
433	1	4	7.06 ,,	200.6	181.1
449	1	10	3.55 10^{-3}	200.5	180.9
453	3	15	2.65 ,,	200.5	180.5
458	1	29	5.12 ,,	200.4	180.9
465	2	33	5.82 ,,	200.3	180.9
472	2	58	9.85 ,,	200.3	180.9
473	1	58	1.02 10^{-2}	200.3	180.9
475	1	67	1.18 ,,	200.2	180.8
477	3	83	1.46 ,,	200.2	180.5
482	5	112	1.98 ,,	200.2	180.4
485	2	140	2.47 ,,	200.1	180.6
487	5	153	2.70 ,,	200.1	180.7
490	1	190	3.36 ,,	200.1	180.6
494	1	271	4.79 ,,	200.1	180.2
500	1	334	5.90 ,,	200.0	180.0
				Average	180.7 ± 0.2^b

[a]Average value of the number of points listed in the second law.
[b]The error is the standard deviation.

by the following equation :

$$\lg P(\text{kPa}) = 12.09 \pm 0.07 - (6652 \pm 34)/T$$

where the associated errors are the standard deviations.

(B) Spectroscopic Study :

The experimental apparatus is that described in details in previous works[11,12]. The infrared spectra of gaseous 6-methyluracil were recorded over the frequency range 100-4000 cm^{-1} with a Perkin-Elmer 180 IR grating spectrophotometer purged with dry nitrogen. Stainless steel cells, 30 cm pathlength, were used. Temperature of the cell was kept around 470 K during the scanning of the spectrum and measured with iron to constantan thermocouple. Nitrogen gas at one atm. was used as diffusion barrier. Temperature was recycled during the experimental runs as a tool of distinguishing among the spectra due to the desired species and the background.

The assignment of thirty-nine normal vibrations was performed comparing the infrared gas phase spectrum of 6-methyluracil with that of gaseous uracil[8] and taking into account the results of a quantum chemical study at CNDO/2 level on the electronic structure of some uracil derivatives[13]. The conclusion of previous vibrational investigations on uracil and some pyrimidine bases[1,8] were also considered in the present assignment. The infrared spectrum of 6-methyluracil can be regarded as the overlap of the vibrations belonging to uracil with the modes of the methyl group. The analysis of the spectrum suggest that our expectations are plentily fulfilled. In this paper we discuss the characteristic features only for sake of brevity since a detailed study on gaseous and matrix isolated uracil will be reported elsewhere[8].

The NH stretching vibrations are attributed to the bands observed at 3415 and 3435 cm^{-1} which positions are in agreement with the calculations performed by Harsanyi *et al*[13] for uracil. The absorption at 3040 cm^{-1} is readily assigned to the νCH stretching while the peaks between 2970 and 2985 cm^{-1} are confidently attributed to the methyl stretching modes.

Both the theoretical calculation[13] and the conclusions of the previous works[1,2] support the identification of the νCO, νCC and νCN stretchings. As regards the νCO motions, the two expected vibrations are recognized in the strong doublet at 1711 and 1724 cm^{-1} while the line at 1620 cm^{-1} can be reasonably related to the νCC vibration. In the region 1300-1480 cm^{-1} three additional bands falling at 1390, 1444 and 1460 cm^{-1} are observed. These absorptions are not present in the gaseous spectrum of uracil and their number and position suggest that they could belong to the methyl deformations. The same argumentations can be reliably employed in the assignment of the bands lying at 955, 660 and 520 cm^{-1} and attributed to the $\nu C-CH_3$ stretching and to the in-plane and out-of-plane $C-CH_3$ deformations. At last, the absorption observed at 1030 cm^{-1} seems most probably due to the methyl rocking mode.

The vibrational analysis foresees three out-of-plane ring torsions. Two of them are assigned to the bands occurring at 127 and 350 cm^{-1} on the

basis of the theoretic expectations[13] which also indicate that the remaining torsion should be expected below 100 cm^{-1}, therefore out of the range of our investigation. The proposed assignment is reported in Table 2.

TABLE 2—GAS PHASE IR SPECTRUM OF 6-METHYLURACIL AND BANDS ASSIGNMENT

Frequency (cm^{-1})	Assignment
3435	NH stretching
3416	" "
3040	CH stretching
2985	methyl stretching
2980	" "
2970	" "
1724	CO stretching
1711	" "
1620	CC stretching
1480	NH deformation
1460	methyl deformation
1444	" "
1415	CN stretching
1390	methyl deformation
1366	NH deformation
1321	NH deformation
1265	CN stretching
1155	CH deformation
1058	CN stretching
1030	methyl rocking
1015	skeletal deformation
955	$C-CH_3$ stretching
940	CN stretching
920	CH out-of-plane deformation
820	CO out-of-plane deformation
744	CC stretching
731	CO out-of-plane deformation
700	CH out-of-plane deformation
660	$C-CH_3$ in-plane deformation
588	skeletal deformation
550	" "
533	CO in-plane deformation
520	$C-CH_3$ out-of-plane deformation
477	NH out-of-plane deformation
460	" "
380	CO in-plane deformation
350	out-of-plane torsion
127	out-of-plane torsion
67[a]	out-of-plane torsion

[a] This frequency is one of the out-of-plane torsions calculated by Csàszàr and Harsànyi for uracil (see paragraph B, ref.[13]

(C) *Thermodynamic Functions* :

In Table 3 the thermodynamic functions of gaseous 6-methyluracil are listed. In order to calculate these functions, the results of the present spectroscopic study are employed to derive the vibrational contribution to the partition function. Bond distances and angles are estimated as follows since no structural data are at present available : the same geometrical parameters of uracil[14] are assumed to hold for 6-methyluracil while the $C-CH_3$ and the CH distances are kept equal to 1.53 and 1.11Å respectively ; the HCH angles of the methyl group are supposed to be tetrahedral. The electronic ground state is taken as $^1\Sigma$ and the contribution to the electronic partition functions reported in this paper are carried out through the usual statistical method[16].

TABLE 3—THERMODYNAMIC FUNCTIONS OF GASEOUS 6-METHYLURACIL

T (K)	S°_T (J/mol K)	$-(G^\circ_T-H^\circ_{298})/T$ (J/mol K)	$(H^\circ_T-H^\circ_{298})$ (kJ/mol)
298.15	339.3	339.3	0.00
300	340.0	339.5	0.15
350	356.7	340.9	5.60
400	373.3	342.2	12.40
450	389.1	345.6	19.60
500	406.0	350.3	27.85
550	420.5	355.2	35.90
600	435.6	361.1	44.70

Conclusion

The vapour pressure of 6-methyluracil determined from torsion effusion measurements permitted to evaluate the second law sublimation ΔH°_{465} = 127±0.6 kJ/mol. At each temperature a value of the third law sublimation ΔH°_{298} was calculated and reported in Table 1, the necessary free energy functions of solid 6-methyluracil were estimated through the heat capacity values of solid uracil[8] corrected for the difference $C^\circ_p(CH_3)-C^\circ_p(H)$[17], those of the gaseous species are determined experimentally (section C). The average third law ΔH°_{298} = 130.6±0.2 kJ/mol (the error is standard deviation) coincides with that derived from the second law ΔH°_{298} = 130.7±0.6 kJ/mol corrected at 298.15 K using the heat content difference ($H^\circ_{465}-H^\circ_{298}$). The heat content of the solid phase was calculated through the estimated C°_p values and those of the gas phase were derived by the $H^\circ_T-H^\circ_{298}$ reported in Table 3.

Even if the agreement between second and third law ΔH°_{298} value is excellent, we believe that the associated error should be about 6 kJ/mol taking into account the uncertainties associated to the temperature measurements, to the calibration factors and to thermodynamic functions estimation of 6-methyluracil (s). So that the value ΔH°_{298} = 131±7 kJ/mol associated to the vaporization process of 6-methyluracil is proposed.

Acknowledgement

Thanks of the authors are due to Prof. V. Piacente for his kind collaboration and to the Ungarian Academy of Sciences for the contribution to this work.

References

1. C. L. ANGELL, *J. Chem. Soc.*, 1961, 504.
2. H. SUSI and J. S. ARD, *Spectrochim. Acta*, 1971, 27A, 1549.
3. S. NUNZIANTE CESARO, private communication.

4. J. M. RICE, G. O. DUDEK and M. BARBER, *J. Amer. Chem. Soc.*, 1965, **87**(20), 4569.
5. G. BARDI, L. BENCIVENNI, D. FERRO, B. MARTINI, S. NUNZIANTE C. and R. TEGHIL, in press on *Thermochim. Acta.*
6. BEILSTEINS, Handbuch der Organishen Chemie, 1936, 24, 312.
7. R. D. FREEMAN, Momentum Sensor in the Characterization of High Temperature Vapours, J. L. MARGRAVE Editor, Wiley. N. Y., 1967.
8. V. PIACENTE and G. DE MARIA, *Ric. Scient.*, 1969, **39**, 549.
9. R. D. FREEMAN and A. W. SEARCY, *J. Chem. Phys.*, 1954, **22**, 762.
10. R. HULTGREEN, R. L. ORR and K. K. KELLEY, Supplement to Selected Values of Thermodynamic Properties of Metals and Alloys, Dept. of Min. Techn. Un. California, Berkeley CA, 1967.
11. L. BENCIVENNI, A. FARINA, B. MARTINI, S. NUNZIANTE CESARO, R. TEGHIL and M. SPOLITI, *J. Mol. Struct.*, fall 1980.
12. L. BENCIVENNI, A. FARINA, S. NUNZIANTE CESARO, R. TEGHIL and M. SPOLITI, *J. Mol. Struct.*, fall 1980.
13. P. CSÁSZÁR and L. HARSÁNYI, private communication.
14. R. F. STEWARE, *Acta Cryst.*, 1967, **23**, 1102.
15. S. J. CYVIN, Molecular Vibrations and Mean Square Amplitudes, Elsevier Publishing Company, N. Y., 1968.
16. G. N. LEWIS and M. RANDALL, Thermodynamics, McGraw Hill Book Company, N. Y., 1970.
17. JANAF, Thermochemical Tables, edited by D. R. STULL and H. PROPLET, NSRDS-NDS-37 (U. S. GPO, Washington, D. C., 1971), 2nd Edition.

J. Indian Chem. Soc.,
Vol. LVII, June 1980, pp. 633-636

Syntheses of Furano Compounds : Part XLIV. Syntheses of 2-Carboxybenzo[b]Furan-3-Acetic Acid and 3-Carboxybenzo[b]Furan-2-Acetic Acid

J. N. CHATTERJEA and RADHIKA PATI SAHAI

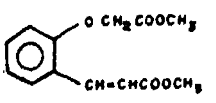
Department of Chemistry, Patna University, Patna-5

Manuscript received 6 September 1979, accepted 9 April 1980

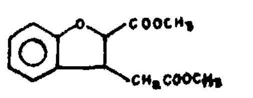
2-Carboxybenzo[b]furan-3-acetic acid and 3-carboxybenzo[b]furan-2-acetic acid have been synthesised. A new synthesis of benzo[b]furan-3-acetic acid, a plant hormone is reported.

THE compounds named in the title were required in a programme aimed at the elaboration of the synthesis of some new heterocyclic systems condensed at the 1, 2-positions of benzo[b]furan. A synthesis of the compounds is described in the present paper.

A synthesis of methyl 2-methoxycarbonylcoumaran-3-acetate(II) by internal Michael reaction on methyl coumarate-O-acetate(I) by adaptation of the work of Koelsch[1] has been achieved.



I

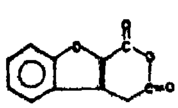


II

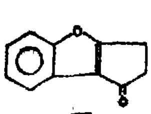
The compound (II) could not be dehydrogenated to compound (IV) by using Pd – C (10%) in *p*-cymene[2]. However, when subjected to allylic bromination with NBS followed by dehydrobromination using N, N-dimethylaniline[3], 2-carboxybenzo-[b]furan-3-acetic acid(III) was obtained.

The dimethyl ester(IV) signalled resonances at τ2.2-2.7 (4H, aromatic protons) ; 6.25, 6.0 (6H, $-COOCH_3$, $-CH_2COOCH_3$) and 5.8 (2H, CH_2COOCH_3).

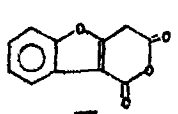
The anhydride(V) of the acid(III) was prepared by reaction with acetyl chloride and this could be converted into the half-ester(VI) by methanolysis. Compound (VI) could also be prepared by controlled hydrolysis of compound (IV). The half-ester on decarboxylation with copper-bronze followed by hydrolysis gave benzo[b]furan-3-acetic acid(VII), a plant hormone[4,5].



V

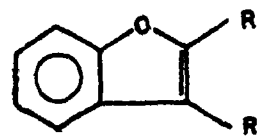


IX



XI

Ethyl coumarilate[6] was converted to benzo[b]-furan-2-carboxaldehyde[7,8] following McFadyen and Stevens' method[9]. The aldehyde when subjected to Doebner's reaction[10] with malonic acid gave benzo[b]furan-2-acrylic acid which, in turn, was quantitatively reduced to benzo[b]furan-2-propionic acid(VIII) with sodium amalgam. This acid on cyclodehydration with P_2O_5 gave 1-oxo-1*H*-benzo[b]-cyclopenteno[2, 3-d]furan(IX). Attempt to prepare 3-carboxybenzo[b]furan-2-acetic acid(XI) from compound (IX) by alkaline oxidation[11] of the related oxalyl derivative with H_2O_2 proved abortive ; the only isolable product was salicylic acid arising by the rupture of the furan ring.



(III) $R=COOH$, $R_1=CH_2COOH$
(IV) $R=COOCH_3$, $R_1=CH_2COOCH_3$
(VI) $R=COOH$, $R_1=CH_2COOCH_3$
(VII) $R=H$, $R_1=CH_2COOH$
(VIII) $R=CH_2CH_2COOH$, $R_1=H$
(X) $R=CH_2COOCH_3$, $R_1=COOC_2H_5$
(XI) $R=CH_2COOH$, $R_1=COOH$

However, 3-ethoxycarbonylbenzo[b]furan-2-carboxylic acid, prepared according to Koelsch and Whitney[12] from ethyl phenoxyacetate and ethyl oxalate, was homologated by Arndt-Eistert procedure[13] to give (X) which was hydrolysed to the acid (XI). This acid also gave the anhydride(XII) on treatment with acetyl chloride.

Experimental

All melting and boiling points are uncorrected. The IR spectra were recorded in Perkin-Elmer Spectrophotometer Model 237. The NMR spectra were recorded in Varian A—60 instrument and in deutero-chloroform with TMS as internal standard

(chemical shifts are expressed in τ values and J in Hz.).

Methyl Coumarate-O-acetate(I) :

A solution of sodium (1.2 g) in dry methanol (17 ml) was treated with coumarin (7.3 g) and boiled for 10 minutes. Methyl bromoacetate (8.0 g) was then added, and boiling continued for 3 hours. The mixture was then poured into ice water (100 ml), which resulted in separation of an oil. It was left overnight and extracted with ether, washed with water and dried (Na_2SO_4). Removal of the solvent afforded a colourless thick oil. Distillation of the oil under reduced pressure (b.p. 172-74°/1.75 mm) gave methyl coumarate-O-acetate (8.5 g) as thick colourless liquid which soon solidified. Crystallisation from methanol gave colourless small needles, m.p. 70°. (Found : C, 62.36 ; H, 5.54. $C_{12}H_{14}O_5$ requires C, 62.39 ; H, 5.64%) ; ν_{max} 1630, 1697 and 1755 cm^{-1}.

Methyl 2-Methoxycarbonylcoumaran-3-acetate(II) :

When a solution of sodium (0.12 g) in dry methanol (2 ml) was added to methyl coumarate-O-acetate (6.5 g) at room temperature, the mixture became yellow and its temperature rose considerably. It was then warmed for 15 minutes, cooled and neutralised with acetic acid. The mixture was extracted with ether, ethereal layer washed with dilute Na_2CO_3 solution, water and dried ($MgSO_4$). Removal of the solvent furnished(II) as a thick colourless oil (5.4 g ; b.p. 151-52°/1.5 mm) which solidified. This was crystallised from methanol in colourless needles, m.p. 55°. (Found : C, 62.29 ; H, 5.48. $C_{12}H_{14}O_5$ requires C, 62.39 ; H, 5.64%) ; ν_{max} 1715 and 1760 cm^{-1} ; NMR($CDCl_3$) : τ 2.77-3.16 (4H, aromatic protons) ; 6.27 (3H, s, $-CH_2COOCH_3$) ; 6.2 (3H, s, $-COOCH_3$) ; 7.22 (2H, d, J=4Hz., $-CH_2COOCH_3$) ; 5.88 (1H, m, $-CHCH_2COOCH_3$) ; 5.05 (1H, d, J=4Hz., $-CHCOOCH_3$).

2-Carboxybenzo[b]furan-3-acetic Acid(III) :

A trace of benzoyl peroxide was added to a mixture of methyl 2-methoxycarbonylcoumaran-3-acetate (1.0 g) and NBS (0.72 g) in dry CCl_4(50 ml) and the resulting mixture heated on a water bath. The colour of the solution gradually became red. After 4 hours of reflux, the red colour was discharged and hydrogen bromide gas began to appear at the condenser outlet. Refluxing was further continued for one more hour. By that time evolution of hydrogen bromide had ceased. The mixture was cooled, filtered and the solvent removed under reduced pressure to obtain a brownish red oil (1.35 g). This was heated for 4 hours with freshly distilled dimethylaniline (16.5 ml) in a metal bath heated at 195-200°. The brownish solution was cooled, taken up in ether and washed thrice with 40 ml portions of well-cooled H_2SO_4(3*N*), water and dried ($MgSO_4$). Removal of the solvent left a brown oil which was refluxed for 5 hours with a solution of aqueous methanolic (1 : 1) potash (1.5 g in 20 ml). Methanol was removed from the reaction mixture and the alkaline solution cooled, diluted with water and extracted with ether. The aqueous solution, thus obtained was cooled and just acidified (conc. HCl) to afford a thick brown oil which was discarded. Addition of four to eight more drops of conc. HCl gave second crop of the oil which was also discarded. Further acidification of the solution afforded 2-carboxybenzo[b]furan-3-acetic acid as a light grey solid (0.6 g). This was recrystallised from acetic acid in light grey needles, m.p. 230° (decomp.). (Found : C, 59.87 ; H, 3.61. $C_{11}H_8O_5$ requires C, 60.00 ; H, 3.66%) ; ν_{max} 1680 and 1720 cm^{-1}.

The dimethyl ester(IV) obtained as a thick oil was distilled (b.p. 165°/1.75 mm) which solidified at room temperature. Crystallisation from benzene-petroleum ether (40-60°) gave cluster of colourless needles, m.p. 88°. (Found : C, 62.88 ; H, 4.69. $C_{13}H_{12}O_5$ requires C, 62.90 ; H, 4.87%) ; ν_{max} 1708 and 1739 cm^{-1}.

2-Carboxybenzo[b]furan-3-acetic Anhydride(V) :

Compound (III ; 0.5 g) was refluxed with acetyl chloride (1 ml) in dry benzene (4 ml) for 4 hours. Removal of the solvent afforded a pale brown solid of the anhydride which on crystallisation from dry benzene was obtained in colourless shining plates, m.p. 199° (decomp.). (Found : C, 65.26 ; H, 3.01. $C_{11}H_6O_4$ requires C, 65.35 ; H, 2.99%) , ν_{max} 1765 and 1800 cm^{-1}.

Methyl 2-Carboxybenzo[b]furan-3-acetate(VI) :

(a) The foregoing anhydride (0.4 g) was refluxed with dry methanol (10 ml) under dry conditions for 4 hours. Removal of the solvent gave the half-ester, crystallised from benzene in cluster of colourless shining needles, m.p. 148°. (Found : C, 61.48 ; H, 4.25. $C_{12}H_{10}O_5$ requires C, 61.54 ; H, 4.30%).

(b) Compound (IV ; 0.5 g) was refluxed with methanolic potash (1 mol ; 1.12 ml ; 10%) for 20 minutes. Colourless solid obtained after removing methanol was taken up in water, washed with ether and acidified (conc. HCl) to yield a colourless precipitate of the half-ester. This was crystallised from benzene in colourless needles, m.p. 148°. (Found : C, 61.37 ; H, 4.16. $C_{12}H_{10}O_5$ requires C, 61.54 ; H, 4.30%) ; ν_{max} 1665 and 1730 cm^{-1}.

Benzo[b]furan-3-acetic Acid(VII) :

The foregoing half-ester (1.17 g) was mixed with copper-bronze (100 mg) and heated in a metal bath

at 150° for 30 minutes till the evolution of CO_2 was complete. The product on distillation under reduced pressure yielded a light yellow oil (0.9 g). This was heated with NaOH (2 ml ; 10%) for 1.5 hours, cooled and acidified (conc. HCl) to furnish a colourless solid of (VII). This was recrystallised from petroleum ether in flattened white needles, m.p. 89-91° (lit.[4,5]). (Found : C, 67.90 ; H, 4.38. Calc. for $C_{10}H_8O_3$: C, 68.18 ; H, 4.58%) ; ν_{max} 1710 cm^{-1}.

Benzo[b]furan-2-propionic Acid (VIII) :

Ethyl coumarilate (3.5 g) was refluxed with hydrazine hydrate (8 ml ; 99%) in ethanol (16 ml) for 5 hours. The hydrazide crystallised from dilute ethanol in colourless needles, m.p. 174°. (Found : N, 15.86. $C_9H_8O_2N_2$ requires N, 15.90%). The hydrazide (2.7 g) in dry pyridine (18 ml) was treated at 0° with tosyl chloride (4.2 g) and after 6 hours the mixture was poured into iced HCl. The tosyl hydrazide derivative separated as cream coloured solid, m.p. 200-201°. (Found : N, 8.36. $C_{16}H_{14}O_4N_2S$ requires N, 8.48%). A solution of the tosyl hydrazide (2.0 g) in ethylene glycol (15 ml) was heated at 160° and anhydrous Na_2CO_3 (3.0 g) added to it in one lot. The vigorous reaction was quenched after 3 minutes by pouring into hot water. The resultant mixture was cooled and extracted with ether to give the benzo[b]furan-2-carboxaldehyde (b.p. 135°/18 mm) (lit.[7,8]). (Found : C, 73.88 ; H, 4.13. Calc for $C_9H_6O_2$: C, 73.96 ; H, 4.14%) ; ν_{max} 1670 cm^{-1}.

The foregoing aldehyde (1.0 g) and malonic acid (1.5 g) in dry pyridine (3.1 ml) with piperidine (1 ml) were heated for 6 hours, cooled, diluted with water and acidified (HCl) to afford benzo[b]furan 2-acrylic acid (1.3 g), crystallised from alcohol in colourless plates, m.p. 221-22°. (Found : C, 70.06 ; H, 4.12. $C_{11}H_8O_3$ requires C, 70.21 ; H, 4.29%) ; ν_{max} 1625 and 1690 cm^{-1}.

The above acid was quantitatively reduced with sodium amalgam (2%) giving benzo[b]furan-2-propionic acid, crystallised from benzene in colourless shining flakes, m.p. 145-46°. (Found : C, 69.30 ; H, 5.18. $C_{11}H_{10}O_3$ requires C, 69.46 ; H, 5.30%) ; ν_{max} 1700 cm^{-1}.

Cyclodehydration : Formation of 1-oxo-1H-benzo-[b]cyclopenteno[2, 3-d]furan (IX) :

This acid (1.4 g) was treated with P_2O_5 (10.0 g) in dry benzene (10 ml) for 10 hours to give the ketone (IX) which crystallised from benzene in cream coloured shining needles, m.p. 1[illegible]5°. (Found : C, 76.72 ; H, 4.65. $C_{11}H_8O_2$ requires C, 76.73 ; H, 4.68%) ; ν_{max} 1700 cm^{-1}.

The 2, 4-dinitrophenylhydrazone was obtained in blood-red needles from acetic acid, m.p. 301° (decomp.). (Found : N, 15.87. $C_{17}H_{12}O_5N_4$ requires N, 15.90%).

Attempted Synthesis of 3-Carboxybenzo[b]furan-2-acetic Acid :

A mixture of (IX ; 0.86 g) and dry ethyl oxalate (0.73 g) was treated with sodium methoxide (from 0.12 g Na) in dry benzene (4 ml) when the colour changed to greenish yellow. The mixture was kept overnight at room temperature resulting in sodium salt of the oxalyl ester which was filtered and treated with KOH (6.0 g) in methanol (30 ml). After 30 minutes, H_2O_2 (15 ml ; 30%) and methanol (20 ml) were added all at once and allowed to stand for further 0.5 hour. After removal of methanol, it was diluted with water and extracted with ether. The aqueous layer was acidified (conc. HCl) and extracted with chloroform. Removal of the solvent afforded a colourless solid, m.p. 159°, which was identified as salicylic acid.

Methyl 3-Ethoxycarbonylbenzo[b]furan-2-acetate (X) :

3-Ethoxycarbonylbenzo[b]furan-2-carboxylic acid (1.4 g) in dry benzene (6 ml) was refluxed with thionyl chloride (2 ml) for 3 hours. The excess of thionyl chloride was then removed under reduced pressure and the last traces removed by twice successive addition of benzene followed by its removal under reduced pressure. The resulting oily (light yellow) acid chloride in dry ether was added to dry ethereal diazomethane (prepared from nitrosomethylurea, 6.0 g) and left overnight in the refrigerator. Next day, ether was removed under reduced pressure to furnish the diazoketone as an orange oil. The diazoketone in dry methanol (30 ml) was heated on a water bath ; to it was added small amount of slurry of silver oxide (0.7 g) in dry methanol (20 ml) and stirred. As soon as the evolution of nitrogen subsided, more of the silver oxide was introduced and this process continued until all the slurry had been added. The mixture was then refluxed for 20 hours. Within this period about 1.4 g of silver oxide was added in instalments. Then the mixture was treated with charcoal, filtered and solvent evaporated to obtain pale yellow oil (0.7 g) (b. p. 130°/0.3 mm) which solidified. Crystallisation from methanol gave pale yellow needles, m.p. 151-52°. (Found : C, 64.02 ; H, 5.41. $C_{14}H_{14}O_5$ requires C, 64.11 ; H, 5.38%) ; ν_{max} 1705 and 1755 cm^{-1}.

3-Carboxybenzo[b]furan-2-acetic Acid(XI) :

The foregoing ester (0.28 g) was heated with NaOH (1 ml ; 10%) for 3 hours, cooled and acidified to furnish compound (XI) in quantitative yield, crystallised from acetic acid in needles, m.p. 242°. (Found : C, 59.95 ; H, 3.63. $C_{11}H_8O_5$ requires C, 60.00 ; H, 3.66%). The anhydride(XII) separated as shining needles from acetyl chloride, m.p. 201-2°. (Found : C, 65.31 ; H, 2.95. $C_{11}H_6O_4$ requires C, 65.35 ; H, 2.99%) ; ν_{max} 1765 and 1790 cm^{-1}.

Acknowledgement

One of us (R.P.S.) is indebted to the U.G.C., New Delhi for providing with a fellowship and the authorities of Bhagalpur University for the study leave.

References

1. C. F. Koelsch ; *J. Amer. Chem. Soc.*, 1945, **67**, 570.
2. D. Rosenthal, P. Grabowich, E. F. Sabo and J. Fried, *J. Amer. Chem. Soc.*, 1963, **85**, 3976.
3. T. A. Geissman and E. Hinreiner, *J. Amer. Chem. Soc.*, 1951, **73**, 786.
4. V. Titoff, H. Müller and T. Reichstein, *Helv. Chim. Acta*, 1937, **20**, 883.
5. E. R. Marshall, J. A. Kuck and R. C. Elderfield, *J. Org. Chem.*, 1942, **7**, 453.
6. A. Hantzsch, *Chem. Ber.*, 1886, **19**, 2401.
7. M. Bisagni, N. P. Buu-Hoi and R. Royer, *J. Chem. Soc.*, 1955, 3689.
8. V. T. Suu, N. P. Buu-Hoi and N. D. Xuong ; *Bull. Soc. Chim.*, France, 1962, 1876.
9. J. S. McFadyen and T. S. Stevens, *J. Chem. Soc.*, 1936, 584.
10. O. Doebner, *Chem. Ber.*, 1900, **33**, 2140.
11. J. Eichenberger, *Helv. Chim. Acta*, 1948, **31**, 1663.
12. C. F. Koelsch and A. G. Whitney, *J. Amer. Chem. Soc.*, 1941, **63**, 1762.
13. F. Arndt and B. Eistert, *Chem. Ber.*, 1935, **68**, 200.

J. Indian Chem. Soc.,
Vol. LVII, June 1980, pp. 637-639

Convenient Preparation of Homophthalic Acids

C. BHAKTA* and SANAT K. MUKHERJEE

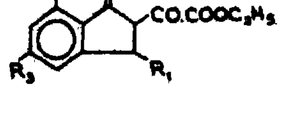
Department of Chemistry, Patna University, Patna 800 005 (India)

Manuscript received 18 December 1979, accepted 13 May 1980

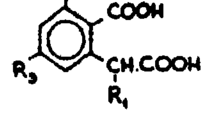
Preparation of homophthalic acids by peroxide oxidation of indan-1-one-2-glyoxalates is reported. Orientation of acetylation of methyl 3, 5-dimethoxyphenylacetate has been established.

INDAN-1-ones are in general converted into homophthalic acids by (i) peroxide oxidation of the related indan-1,2-diones[1-3]; (ii) Beckmann rearrangement of 2-oximino derivatives[4] and (iii) direct oxidation with chromic acid[5]. The synthesis of 3,5-dimethoxyhomophthalic acid, however, admitted of exploration of a more satisfactory route and it is now found that indan-1-ones may smoothly be converted into homophthalic acids by peroxide oxidation of the related 2-glyoxalates[6] in alkaline medium. The method appears general (*vide* experimental) and 3,5-dimethoxyhomophthalic acid was isolated in 50% yield.

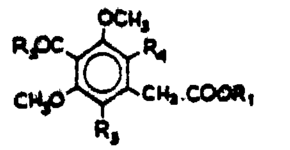
A different synthesis of 3,5-dimethoxyhomophthalic acid was attempted from methyl 3,5-dimethoxyphenyl acetate by way of the Friedel-Craft acetylation which took place para to the acetate moiety. Hypobromite oxidation of the ketone afforded 4-carboxy-3,5-dimethoxyphenylacetic acid which appears identical with that of Jerdan[7] although no direct comparison could be made. The orientation is established in the following manner: (a) the dicarboxylic acid or the related dichloro acid (*vide* experimental) could not be converted into an anhydride with acetic anhydride or acetyl chloride; (b) the related dichloro ester, obtained by chlorination of the ester(VIII) with sulphuryl chloride[8], on formylation[9] with methyl formate afforded an α-formyl derivative which could not be cyclised into an isocoumarin. In agreement, Jerdan reported similar results with his acid prepared by an entirely different method.



(I) $R_1 = H, R_2 = R_3 = OCH_3$
(II) $R_1 = C_6H_5, R_2 = R_3 = H$



(III) $R_1 = R_2 = R_3 = H$
(IV) $R_1 = H, R_2 = R_3 = OCH_3$
(V) $R_1 = C_6H_5, R_2 = R_3 = H$



(VI) $R_1 = R_2 = CH_3, R_3 = R_4 = H$
(VII) $R_1 = H, R_2 = OH, R_3 = R_4 = H$
(VIII) $R_1 = CH_3, R_2 = OCH_3, R_3 = R_4 = H$
(IX) $R_1 = CH_3, R_2 = OCH_3, R_3 = R_4 = Cl$
(X) $R_1 = H, R_2 = OH, R_3 = R_4 = Cl$

Experimental

All melting and boiling points are uncorrected. Infrared spectra were recorded in Perkin-Elmer spectrophotometer, model 237.

Homophthalic Acid(III): A solution of indan-1-one (1.32 g) and ethyl oxalate (2.2 g) in dry benzene (15 ml) was added dropwise over fifteen minutes to dry sodium methoxide (prepared from 0.45 g sodium) at 0° and then left overnight. The solid sodium salt, which separated, was collected and added to a solution of potassium hydroxide (5 g) in methanol (25 ml). The mixture was allowed to stand for thirty minutes and then a mixture of 30% hydrogen peroxide (10 ml) and methanol (25 ml) was added to it all at once. The mixture, after allowing it to stand for one hour, was refluxed for 2 hours. The residue, after removal of solvent, was dissolved in water (50 ml) and extracted with ether (2 × 100 ml). The aqueous layer was acidified with concentrated hydrochloric acid to give homophthalic acid (0.8 g), m.p. 179-80°, mixed m.p. with authentic sample undepressed.

Ethyl 5,7-dimethoxyindan-1-one-2-glyoxalate(I): A solution of 5,7-dimethoxyindan-1-one (0.92 g) and ethyl oxalate (1 g) in dry benzene (15 ml) was treated similarly with sodium methoxide (from 0.2 g sodium) to give solid sodium salt (0.8 g). Acidification of the sodium salt afforded the *ester*(I) (0.6 g)

* For correspondence.

which was crystallised from ethanol in yellow crystals, m.p. 192-93°; IR(KBr): 1730 and 1695 cm^{-1}. (Found: C, 61.4; H, 5.3; $C_{16}H_{18}O_6$ requires C, 61.6; H, 5.5%). It gives green colouration with ferric chloride solution.

3,5-Dimethoxyhomophthalic Acid(IV): The foregoing sodium salt (0.5 g) was added to a solution of potassium hydroxide (2 g) in methanol (15 ml) and allowed to stand for half an hour. The mixture was then treated with a mixture of 30% hydrogen peroxide (4 ml) and methanol (10 ml) as described earlier and worked up as usual to give 3,5-dimethoxyhomophthalic acid(IV), which was crystallised from benzene in colourless needles (0.3 g), m.p. 171-72° (lit.[8], m.p. 172-73°).

Ethyl 3-phenylindan-1-one-2-glyoxalate(II): 3-Phenylindan-1-one (0.4 g), ethyl oxalate (0.45 g) and sodium methoxide (prepared from 0.1 g sodium) was treated in an analogous manner as described for (I) to give the ester (II) which crystallised from benzene-petroleum ether as colourless crystals (0.3 g), m.p. 127-28°; IR(KBr): 1735, 1690 and 1655 cm^{-1}. (Found: C, 73.9; H, 5.0; $C_{19}H_{16}O_4$ requires C, 74.0; H, 5.2%). It gave violet colouration with ferric chloride solution.

α-Phenylhomophthalic Acid(V): The sodium salt of the foregoing compound (0.2 g) was added to a solution of potassium hydroxide (1 g) in methanol (8 ml) and allowed to stand for half an hour and then treated with a mixture of 30% hydrogen peroxide (2 ml) and methanol (5 ml) in the same way as described for the preparation of homophthalic acid. On working up in the usual manner, α-phenylhomophthalic acid(V) was obtained which crystallised from benzene in colourless needles (0.12 g), m.p. 159-60° (lit.[10], m.p. 156.5-58.5°); no depression in mixed m.p. with authentic sample.

Methyl 4-acetyl-3,5-dimethoxyphenyl Acetate(VI): To the ice-cold solution of methyl 3,5-dimethoxyphenylacetate[11] (1.0 g) in dichloromethane (5 ml) was added acetyl chloride (3.4 ml) and then finely divided aluminium chloride (1 g) in several instalments with shaking. The mixture was then left overnight in a refrigerator. This was worked up in the usual manner to give *methyl 4-acetyl-3,5-dimethoxyphenylacetate*(VI) (0.8 g), b.p. 192-94/0.3 mm; IR(nujol): 1739 (ester carbonyl) and 1672 cm^{-1} (keto carbonyl); (Found: C, 61.7; H, 6.1. $C_{13}H_{16}O_5$ requires C, 61.9; H, 6.4%).

4-Carboxy-3,5-dimethoxyphenylacetic Acid(VII): The above ketone (1.5 g) was added slowly to a stirred ice-cold solution of hypobromite prepared from bromine (2.9 g) and 10% sodium hydroxide (20 ml) and stirred at this temperature for half an hour, then at room temperature for an hour and finally at 60° for four hours. The mixture was then cooled, saturated sodium bisulphite solution (5 ml) was added and then acidified with concentrated hydrochloric acid to give the *acid*(VII) (0.5 g) which crystallised from benzene as crystalline solid, m.p. 176-78°. (Found: C, 54.9; H, 5.3. $C_{11}H_{12}O_6$ requires C, 55.0; H, 5.0%). The *dimethyl ester* (VIII) boiled at 155-65°/5 mm. (Found: C, 58.1; H, 5.8. $C_{13}H_{16}O_6$ requires C, 58.2; H, 6.0%).

The Ester(IX): The foregoing ester(VIII) (4 g) in dry carbon tetrachloride (250 ml) was treated with sulphuryl chloride (4.3 g) in dry carbon tetrachloride (75 ml) at 0°. A few crystals of benzoyl peroxide was added to it and the mixture kept in a refrigerator for 72 hours. After usual work up, the *dichloro compound* (IX) (2.5 g) was obtained which crystallised from benzene petroleum ether as colourless prisms, m.p. 141°; IR(KBr): 1735 (aliphatic ester carbonyl) and 1721 cm^{-1} (aromatic ester carbonyl). (Found: C, 46.0; H, 3.8. $C_{13}H_{14}O_6Cl_2$ requires C, 46.3; H, 4.16%). The related *dicarboxylic acid*(X) crystallised from acetic acid in colourless needles, m.p. 216°; IR(KBr): 1718 cm^{-1} (carboxyl). (Found: C, 42.6; H, 3.3. $C_{11}H_{10}O_6Cl_2$ requires C, 42.7, H, 3.2%).

Formylation of (IX): A solution of the diester (IX) (0.5 g) in dry ether was added slowly to dry sodium methoxide (prepared from 0.1 g sodium). Methyl formate (5 ml) was then added and the mixture was left overnight in refrigerator. Next day, it was refluxed for one hour. The mixture was then cooled and the aqueous layer was acidified with concentrated hydrochloric acid and worked up as usual to give *dimethyl 2,6-dichloro-4-carbomethoxy-3,5-dimethoxyphenyl-α-formyl acetate* (0.2 g), which crystallised from acetic acid in colourless needles, m.p. 195°; IR(KBr): 1710, 1700 and 1690 cm^{-1}. (Found: C, 45.8; H, 3.6. $C_{14}H_{14}O_7Cl_2$ requires C, 46.0; H, 3.8%).

Acknowledgement

The authors are thankful to Prof. J. N. Chatterjea, Head of the Department of Chemistry, Patna University, Patna, for his keen interest and helpful discussion.

References

1. H. L. SLATES, S. WEBER and N. L. WENDLER, *Chim.*, 1967, 21, 468.
2. F. M. HAUSER and R. P. RHEE, *J. Org. Chem.*, 1977, 42, 4155.

3. J. Mukherjee, J. N. Chatterjea and S. C. Sengupta, *Indian J. Chem.*, 1975, 13, 859.

4. J. V. Brown and G. Kirschbaum, *Ber.*, 1913, 46, 3045.

5. C. K. Ingold and H. A. Piggott, *J. Chem. Soc.*, 1923, 123, 1497.

6. J. Eischenberger, *Helv. Chim. Acta.*, 1948, 31, 1863.

7. D. S. Jerdan, *J. Chem. Soc.*, 1899, 75, 808.

8. J. N. Chatterjea and W. B. Whalley, *J. Chem. Soc.*, 1955, 4127.

9. W. Dieckmann and W. Meiser, *Chem. Ber.*, 1908, 41, 3253.

10. A. Marrili, *Ann. Chim.*, 1962, 52, 3.

11. O. C. Musgrave, *J. Chem. Soc.*, 1957, 1107.

J. Indian Chem. Soc.,
Vol. LVII, June 1980, pp. 640-642

Use of Potassium Bromate : Bromination of Halobenzenes and Halobenzoic Acids

AMALENDU BANERJEE, GOPAL CHANDRA BANERJEE, SACHCHIDANANDA DUTT
(MRS.) SANTA BANERJEE[a] and HARAPRASAD SAMADDAR[b]

Chemistry Department, Jadavpur University, Calcutta-700 032

Manuscript received 24 September 1979, accepted 13 May 1980

Syntheses of bromo compounds by the bromination of halobenzenes and halobenzoic acids using potassium bromate under acidic condition have been discussed.

THE bromination of aromatic compounds still holds its charm to the synthetic organic chemists as is evident from the recent works of Mckillop and Bromley[1]. The use of potassium bromate under acidic condition for oxidation of benzaldehyde[2] as well as bromination of benzoic acid[3] and benzene[4] has been reported. This method is economical, time saving, simple and avoids the possible hazards of using elemental bromine. It involves the dropwise addition of an aqueous solution of potassium bromate to the boiling mixture of the benzene derivatives in (8*N*) sulphuric acid with or without glacial acetic acid for approximately one and a half hours. Only trace of bromine is evolved in most of the cases. Derbyshire and Waters[5] used elemental bromine and potassium bromate as catalyst for similar bromination. The reaction mixture is worked up by the method described before[3,4]. Thus, chlorobenzene has been brominated to furnish a mixture containing 1-bromo-4-chlorobenzene (80%) and 1-bromo-2-chlorobenzene (20%). 1,4-dichlorobenzene gives two products viz. 1-bromo-2,5-dichlorobenzene and very small amount of an unidentified compound, m.p. 147°, whereas 1,4-dibromobenzene produces only 1,2,4-tribromobenzene (30%). The expected 5-bromo-2-chlorobenzoic, 4-bromo-3-chlorobenzoic and 3-bromo-4-chlorobenzoic acids are obtained in fair yields from 2-chlorobenzoic, 3-chlorobenzoic and 4-chlorobenzoic acids respectively. Also 2,5-dibromobenzoic acid is obtained from 2-bromobenzoic acid and the same product 3,4-dibromobenzoic acid is obtained from both 3-bromo[3] and 4-bromobenzoic acids in similar yields. It is observed that the use of acetic acid as solvent improves the yields of the desired bromo-products and in each case unreacted starting material can be recovered. Iodobenzene furnishes 1-bromo-4-iodobenzene under similar condition with probably iodoxybenzene as an additional product and 2-iodobenzoic acid produces probably 2-iodoxybenzoic acid. Further work in this line is in progress.

Experimental

A.R. acetic acid was heated under reflux for six hours with excess of potassium dichromate and distilled just before use. Pure potassium bromate, sulphuric acid and distilled water were used whenever needed. Gas liquid chromatography was carried out with a Hewlett Packard 5730 A gas chromatograph with flame ionisation detector using H.P. recorder model 7127A. Resolution was performed on a stainless steel column (1.83 m × 3 mm of 3% of SE – 52 on sil. RUB (100-120 mesh) at 180°. The N.M.R. spectra have been mostly taken in 90 MH_z.

1. General Procedure for the Bromination of Halobenzenes :

Potassium bromate solution (10 ml of water per g of the reagent) was added dropwise in course of thirty minutes to the boiling mixture of the required amount of sulphuric acid (8*N*), distilled glacial acetic acid and the halobenzene. The reaction mixture was further heated under reflux for one hour, cooled and poured onto iced-water. The organic material was extracted with chloroform, washed successively with water ; saturated solution of sodium bicarbonate and water, dried over anhydrous sodium sulphate and the solvent was removed from a steam bath. The residue, on fractional distillation under reduced pressure, furnished the bromohalobenzene. Thus, the following compounds were prepared :

(A) *1-Bromo-4-chlorobenzene and 1-bromo-2-chlorobenzene :* Distilled chlorobenzene (22.5 g), glacial acetic acid (200 ml), sulphuric acid (8*N* ; 160 ml) and potassium bromate (16.7 g in 160 ml of water) after the aforementioned reaction condition yielded a gummy yellow oil (20.0 g), b.p. 193°, which on crystallisation from ethanol furnished

(a) Chemistry Department, Dinabandhu Andrews College, Garia, 24-Parganas, West Bengal.

(b) Chemistry Department, Ramakrishna Mission Residential College, Narendrapur, 24-Parganas, West Bengal ; Teacher Fellow (U. G. C.), Chemistry Department, Jadavpur University, Calcutta-700 032.

colourless flakes (10.0 g ; 52%) of 1-bromo-4-chlorobenzene, m.p. 67°[6a], [δ(CCl_4), 7.20 ($H_{3,5}$, d ; J=7Hz) and 7.43 ($H_{2,6}$, d ; J=7Hz) p.p.m.]. After separation of the *para* compound, the mother liquor afforded a liquid (9.5 g), b.p. 82°/10 mm. The vapour phase chromatography of this material revealed the presence of the *ortho* isomer when compared with the pure *para* compound and it indicated the formation of a mixture containing 20% *ortho* and 80% *para* isomer in the overall bromination step.

(B) *2-Bromo-1,4-dichlorobenzene* : A mixture of 1,4-dichlorobenzene (29.4 g), distilled glacial acetic acid (200 ml), sulphuric acid (8*N* ; 170 ml) and potassium bromate (16.7 g in 170 ml of water) after refluxing for ninety minutes followed by usual working up furnished (i) starting material (17.8 g), b.p. 175-180°, (ii) the desired material as a yellowish oil (9.8 g ; 43%), b.p. 79-80°/1 mm, [δ(CCl_4), 7.22 (H_5, d, d ; J=2, 7Hz), 7.37 (H_6, d ; J=7Hz) and 7.65 (H_3, d ; J=2Hz) p.p.m.] and a small amount of pot-residue which on boiling with activated charcoal in ethanol yielded needles, m.p. 147°, (to be investigated further).

(C) *1,2,4-Tribromobenzene* : Pure 1,4-dibromobenzene (4.7 g, m.p. 87°), glacial acetic acid (25 ml), sulphuric acid (8*N* ; 16 ml) and potassium bromate (1.67 g in 16 ml of water) under similar condition furnished a viscous liquid (0.9 g ; 30%), b.p. 100-105°/3 mm, which solidified on cooling and crystallised from ethanol as needles, m.p. 44°[6b], m/e 312, 314, 316, 318 (M^+), 233, 235, 237 (M-Br), 154, 156 (M-2Br). The starting material was recovered as a forerun during the distillation (3.9 g) b.p. 210-220°, which solidified on cooling, m.p. 87°[7a].

(D) *1-Bromo-4-iodobenzene* : A mixture of distilled iodobenzene (40.8 g), glacial acetic acid (200 ml), sulphuric acid (8*N* ; 170 ml) and potassium bromate (16.7 g in 170 ml of water) after ninety minutes' refluxing produced (i) chloroform soluble product and (ii) chloroform insoluble product. The former, after the usual work up and removal of the solvent, furnished unreacted iodobenzene (12.8 g), b.p. 185-190°[7a] and an oil (7.0 g), b.p. 102°/2 mm, which on boiling with ethanol and activated charcoal produced colourless flaky crystals of 1-bromo-4-iodobenzene (6.3 g ; 23%), m.p. 92°[6b], m/e 282, 284 (M^+), 155, 157 (M-I). The aqueous layer, obtained after the extraction with chloroform, was found to deposit large amount of silky white precipitate which on filtration followed by successive washing with water, saturated aqueous sodium bicarbonate solution and alcohol produced a colourless solid (5.5 g ; 16%), m.p. 222° (decomposed with explosion). This material, presumably iodoxybenzene[6b], was estimated[8] to be of 95% purity. This is under further investigation. When acetic acid was omitted in this experiment, the yield of the probable iodoxy compound increased to 32% while the yield of the desired bromo compound remained unchanged.

2. *General Procedure for the Bromination of Halobenzoic Acids* :

The following bromohalobenzoic acids were obtained by the aforementioned method and the cold reaction mixture was poured onto iced-water and usually worked up with chloroform to furnish acidic material which was weighed (to calculate the approximate extent of bromination) and esterified with ethanol and concentrated sulphuric acid in the usual way. The crude mixture of esters, thus obtained, was worked up and distilled under reduced pressure to separate into its components. The esters were subsequently hydrolysed to isolate the starting acids and the bromoderivatives for their identification.

(E) *5-Bromo-2-chlorobenzoic Acid* : A mixture of 2-chlorobenzoic acid (10.0 g), sulphuric acid (8*N* ; 100 ml) and glacial acetic acid (25 ml) was heated under reflux for ninety minutes with the dropwise addition of potassium bromate (8.4 g in 100 ml of water). The resulting crude acid (11.8 g ; the increase in weight indicated 40% bromination) was esterified and worked up in the usual way to furnish (i) low boiling fraction (8.8 g), b.p. 102-4°/1 mm, [δ (CCl_4), 1.40 (CH_2*CH_3*, t ; J=7Hz), 4.37 (*CH_2*CH_3, q ; J=7Hz), aromatic H at 7.23 (H_3, d, d ; J=2, 7 Hz), 7.40 ($H_{4,5}$, complex, m) and 7.79 (H_6, d ; J=d, 2, 7 Hz) p.p.m.] which on hydrolysis with potassium hydroxide produced an acid, m.p. 137° ; m.m.p. with authentic 2-chlorobenzoic acid[7b] remained undepressed and (ii) the desired material (4.5 g ; 27%), b.p. 128-30°/1 mm, [δ (CCl_4), 1.40 (CH_2*CH_3*, t ; J=7Hz), 4.33 (*CH_2* CH_3, q ; J=7Hz) ; aromatic H at 7.27 (H_3, d ; J=7Hz), 7.50 (H_4, d, d ; J=2, 7Hz) and 7.90 (H_6, d ; J=2Hz) p.p.m.] which on alkaline hydrolysis in the usual way gave 5-bromo-2-chlorobenzoic acid[9a], m.p. 155-6°, Neutral Equivalent (N.E.) was found to be 233±3. The acid could not be decarboxylated in the usual way.

(F) *4-Bromo-3-chlorobenzoic Acid* : In a similar method 3-chlorobenzoic acid (7.8 g), sulphuric acid (8*N* ; 120 ml), acetic acid (50 ml) and potassium bromate (12.6 g in 120 ml of water) yielded the crude acid 10.0 g ; 55% conversion), which was esterified, worked up and distilled under reduced pressure to yield (i) low boiling ester (3.7 g), b.p. 104-14°/1 mm, [δ (CCl_4), 1.38 (CH_2*CH_3*, t ; J=7Hz), 4.35 (*CH_2* CH_3, q ; J=7Hz), 7.42 ($H_{4,5}$, m ; complex), 7.90 (H_6, d, d ; J=8, 2 Hz) and 7.97 (H_2, t ; J=2-3 Hz) p.p.m.] which on alkaline hydrolysis produced an acid, m.p. 157-8°, m.m.p. with authentic 3-chlorobenzoic acid[7b] remained undepressed, and (ii) high boiling bromo ester (4.9 g ; 39%), b.p. 133°/1 mm, [δ (CCl_4), 1.41 (CH_2 *CH_3*, t ; J=7Hz), 4.38 (*CH_2* CH_3, q ; J=7Hz), 7.29 (H_6, d, d ; J=2, 7 Hz), 7.60 (H_5, d ; J=7Hz) and 7.77 (H_2, d ; J=2Hz) p.p.m.] which on hydrolysis

produced 4-bromo-3-chlorobenzoic acid[9a], m.p. 218°, N.E. 230±5, in excellent yield.

(G) *3-Bromo-4-chlorobenzoic Acid :* 4-Chlorobenzoic acid (10.0 g), sulphuric acid (8*N* ; 250 ml), acetic acid (50 ml) and potassium bromate (25.0 g in 250 ml of water) furnished the crude acid (12.0 g ; 40% conversion) which was esterified, worked up and distilled to produce (i) ester of the starting acid (8.1 g), b.p. 95-97°/1 mm, [δ (CCl_4), 1.39 (CH_2 $\mathit{CH_3}$, t ; J=7H_z), 4.34 ($\mathit{CH_2}$ CH_3, q ; J=7 H_z), 7.34 ($H_{3,5}$, d, d ; J=2, 9 H_z) and 7.92 ($H_{2,6}$, d, d ; J=2, 9 H_z) p.p.m.] which on hydrolysis furnished the unreacted acid[7b], m.p. 236° and (ii) high boiling bromo ester (3.6 g ; 22%), b.p. 125-27°/mm, [δ (CCl_4), 1.40 (CH_2 $\mathit{CH_3}$, t ; J=7H_z), 4.34 ($\mathit{CH_2}$ CH_3, q ; J=7H_z), 7.41 (H_5, d ; J=7H_z), 7.86 (H_6, d, d ; J=2, 7H_z) and 8.21 (H_2, d ; J=2H_z) p.p.m.] which on hydrolysis produced in good yield, 3-bromo-4-chlorobenzoic acid[9a], m.p. 214°, N.E. 233±3.

(H) *2,5-Dibromobenzoic Acid :* Similarly 2-bromobenzoic acid (4.0 g), sulphuric acid (8*N* ; 35 ml), acetic acid (50 ml) and potassium bromate (3.5 g in 35 ml of water) gave the crude acid (4.8 g ; 51% conversion) which was esterified, worked up and distilled to produce (i) a low boiling ester (1.3 g), b.p. 124-30°/6 mm, [δ (CCl_4), 1.38 (CH_2 $\mathit{CH_3}$, t ; J=7H_z), 4.32 ($\mathit{CH_2}$ CH_3, q ; J=7H_z), 7.27-7.77 (4H ; aromatic ; m) p.p.m.] which on hydrolysis produced 2-bromobenzoic acid[7b], m.p. 150°, m.m.p. with starting material remained undepressed, and (ii) the desired high boiling fraction (2.5 g ; 43%), b.p. 153°/4 mm, [δ (CCl_4), 1.40 (CH_2 $\mathit{CH_3}$, t ; J=7H_z), 4.36 ($\mathit{CH_2}$ CH_3, q ; J=H_z), 7.43 ($H_{3,4}$; complex, m) and 7.83 (H_6, d ; J=2H_z) p.p.m.] which on hydrolysis produced 2,5-dibromobenzoic acid[9b], m.p. 157°, N.E. 275±5.

(I) *3,4-Dibromobenzoic Acid :* Potassium bromate (12.5 g in 125 ml of water) was added dropwise to a refluxing mixture of 4-bromobenzoic acid (8.0 g), sulphuric acid (8*N*; 125 ml) and glacial acetic acid (100 ml). The crude acid (9.4 g ; 46% conversion) thus obtained, was esterified and worked up to furnish (i) ethyl 4-bromobenzoate (3.9 g), b.p. 137°/5 mm, [δ (CCl_4), 1.38 (CH_2 $\mathit{CH_3}$, t ; J=7H_z), 4.35 ($\mathit{CH_2}$ CH_3, q ; J=7H_z), 7.53 ($H_{3,5}$, d ; J=8H_z) and 7.83 ($H_{2,6}$, d ; J=8H_z) p.p.m.] which on hydrolysis produced the starting 4-bromobenzoic acid[7b] m.p. 251°, and (ii) high boiling dibromo ester (4.2 g ; 34%) b.p. 149°/3 mm., [δ (CCl_4), 1.37 (CH_2 $\mathit{CH_3}$, t ; J=7H_z), 4.33 ($\mathit{CH_2}$ CH_3, q ; J=7H_z), 7.62 (H_5, d), 7.66 (H_6, d, d ; J=2, 9H_z) and 8.18 (H_2, d ; J=2H_z), p.p.m.] which on hydrolysis produced 3,4-dibromobenzoic acid[9b] in good yield, m.p. 234°, N. E. 276±5, m.m.p. with the authentic 4-bromobenzoic acid, prepared by neutral permanganate oxidation of *p*-bromo-toluene, was found to be 200-213° with previous shrinking at 190° and with authentic 3,4-dibromobenzoic acid[8] remained undepressed.

(J) *2-Iodoxybenzoic Acid :* Potassium bromate (8.4 g in 85 ml of water) was added dropwise to the refluxing mixture of 2-iodobenzoic acid (13.5 g), sulphuric acid (8*N* ; 85 ml) and glacial acetic acid (50 ml). The reaction mixture was heated under reflux for ninety minutes and attempted to work up with chloroform in the usual way but the acidic product was insoluble in chloroform. This was filtered through Buchner funnel and air-dried to furnish an acid (14.0 g), m.p. 222° (decomposed with explosion) ; N. E. 278±2. This is under further investigation.

Acknowledgement

The authors are thankful to Prof. (Mrs.) K. K. Rohatgi-Mukherjee, Head of the Department of Chemistry, Jadavpur University, Calcutta-700 032, for laboratory facilities and Dr. A. Mukherjee, Department of Macromolecules, I.A.C.S., Calcutta-700 032 and Prof. U. R. Ghatak, Chemistry Department, I.A.C.S., Calcutta-700 032 for some of the spectra and helpful discussion. The award of the Teacher Fellowship to one of us (H.S.) by the University Grants Commission is gratefully acknowledged.

References

1. A. McKillop and D. Bromley, *J. Org. Chem.*, 1972, 37, 88.
2. A. Banerjee, (Mrs.) S. Banerjee and H. Samaddar, *J. Indian Chem. Soc.*, 1979, 56, 985.
3. A. Banerjee, (Mrs.) S. Banerjee and H. Samaddar, *J. Indian Chem. Soc.*, 1976, 56, 988.
4. A. Banerjee, (Mrs.) S. Banerjee, G. C. Banerjee and H. Samaddar, *J. Indian Chem. Soc.*, 1979, 56, 518.
5. D. H. Derbyshire and W. A. Waters, *J. Chem. Soc.*, 1950, Part-I, 578.
6. E. H. Rodd in "Chemistry of Carbon Compounds", Elsevier Publishing Company, Amsterdam, 1954, Vol. IIIA, (a) p. 121, (b) p. 120.
7. H. T. Clarke in "A Hand Book of Organic Analysis, Qualitative and Quantitative", First Indian Edition, Orient Longmans Ltd., 1966, (a) p 176, (b) p. 188-189.
8. H. J. Lucas and E. R. Kennedy, *Org. Syn.*, *Coll.*, 1955, Vol. 3, p. 484.
9. I. Heilbron in "Dictionary of Organic Compounds", 4th Edition, Eyre and Spottiswoode (Publishers) Ltd., London, 1965, Vol. I, (a) p. 428, (b) p. 911.

J. Indian Chem. Soc.,
Vol. LVII, June 1980, pp. 643-645

4,4′-*Bis*-5-Pyrazolones and Their 4,4′-Unsaturated Products for Possible Use as Fungicides

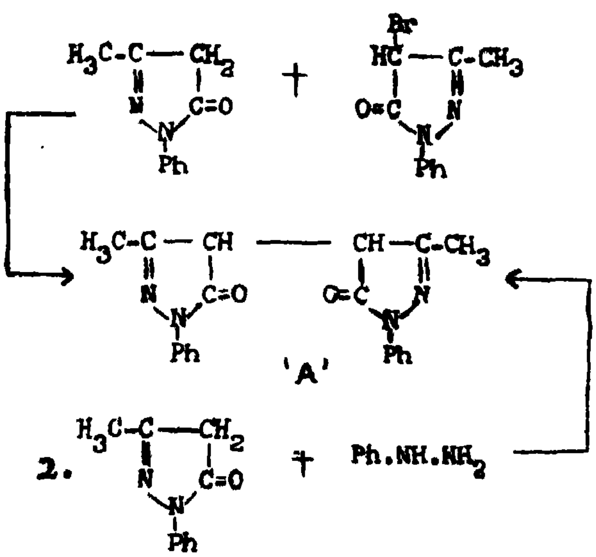
A. NAYAK and A. S. MITTRA

Mayurbhanj Chemical Laboratory, Ravenshaw College, Cuttack-753 003

Manuscript received 6 April 1978, revised 28 March 1980, accepted 13 May 1980

4, 4′-*Bis*-2-pyrazolin-5-ones were prepared by condensing 3-methyl-4-bromo-5-pyrazolones with 2-pyrazolin-5-ones or its 4-nitroso derivatives. Some of these *bis*-derivatives were converted into $C_{4,4'}$ unsaturated compounds. All these compounds have been screened for their antifungal activity against the rice blast pathogen *Pyricularia oryzae* and the brown leaf spot pathogen *Helminthosporium oryzae*. Most of the compounds exhibit significant fungicidal activity and are comparable with the standard fungicides like o-Ethyl-S, S-diphenyl phosphoro dithioate (Hinosan 50%) EC, Difolatan 50% WP and Derosal 60% WP.

IN continuation of our earlier work on heterocyclic fungicides[1-8] containing the 5-pyrazolone ring, it was considered of interest to study the fungitoxicity of the 4, 4′-*bis* compounds obtained by joining two active 5-pyrazolone nuclei and corresponding $C_{4,4'}$ unsaturated ($-C_4=C_{4'}-$) derivatives. This has been accomplished by condensing 5-pyrazolone with 4-bromo-5-pyrazolone so as to obtain the *bis*-compound in which the two nuclei are linked together at $C_{4,4'}$ position by a single bond. The formation of the *bis*-compound (A) was confirmed by comparing it with the *bis*-compound prepared by the standard method[9], which involves refluxing of 5-pyrazolone with phenyl hydrazine.



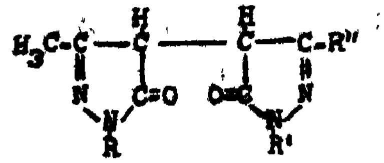
The standard method could not be applied for the fusion of two dissimilar pyrazolone nuclei but this has been accomplished by adopting our present method.

It has also been reported by us[1] that introduction of a nitroso group at 4-position of 5-pyrazolone ring enhances the fungicidal activity considerably against the pathogens *Pyricularia oryzae* and *Helminthosporium oryzae*. So it was thought worthwhile to introduce a nitroso group into one of the two pyrazolone nuclei of the *bis*-compound. This has been achieved by condensing 4-bromo-5-pyrazolone with the 4-nitroso derivative of 5-pyrazolone.

Oxidation of the *bis*-compound in which $-CH-CH-$ linkage at $C_{4,4'}$ position was turned into $-C=C-$ was done with a view to study and compare the fungitoxicity of the oxidation products with that of the parent *bis*-compound. The alkaline solution of the *bis*-compound was treated with a saturated solution of iodine in potassium iodide to produce the oxidation product[10]. This oxidation was also done by treating the *bis*-compound with nitric acid. The stereoisomerism of these 4, 4′-*bis*-saturated and unsaturated pyrazolones was not investigated.

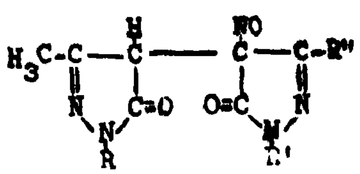
These compounds were tested for their antifungal activity against the pathogens *Pyricularia oryzae* and *Helminthosporium oryzae* following the standard method[11]. All the compounds (Tables 1 and 2) exhibited pronounced fungicidal activity against *P. oryzae*. *Bis*-compounds (1, 5, 6, 8 and 14) and C_4-nitroso *bis*-compounds (17, 20 and 24) showed 100% spore germination inhibition against *P. oryzae*. All these compounds except 1 and 9 were active against *H. oryzae* and one C_4-nitroso compound(17) showed 100% germination inhibition against *H. oryzae*. Fungitoxicity against both the pathogens was not marked for the oxidation products (Table 3) except for compound (33) which exhibited 78% germination inhibition against *P. oryzae* only.

TABLE 1



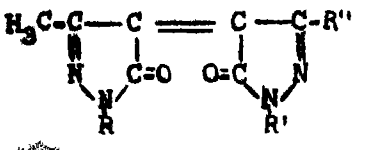
Sl. No.	Nature of R	Nature of R'	Nature of R''	M.P. °C	% Germination inhibition at 1000 ppm conc. *P. oryzae*	*H. oryzae*
1	2	3	4	5	6	7
1.	C_6H_5	C_6H_5	CH_3	320(d)	100	55
2.	C_6H_5	H	CH_3	306	95	70
3.	C_6H_5	$C_6H_4NO_2$(p-)	C_6H_5	225	96	68
4.	C_6H_5	H	C_6H_5	216	99	74
5.	C_6H_5	$C_6H_3(NO_2)_2$(2,4-)	C_6H_5	172	100	62
6.	C_6H_5	$C_6H_3(NO_2)_2$(2,4-)	CH_3	165	100	68
7.	C_6H_5	$CONH_2$	CH_3	305	85	65
8.	C_6H_5	$C_6H_3(NH_2)_2$(2,4-)	CH_3	212	100	68
9.	H	H	CH_3	322(d)	88	85
10.	H	C_6H_5	CH_3	306	94	70
11.	H	$C_6H_4NO_2$(p-)	C_6H_5	282	78	62
12.	H	H	C_6H_5	323	92	65
13.	H	$C_6H_3(NO_2)_2$(2,4-)	C_6H_5	230	92	76
14.	H	$C_6H_3(NO_2)_2$(2,4-)	CH_3	146	100	88
15.	H	$CONH_2$	CH_3	261	62	63
16.	H	$C_6H_3(NH_2)_2$	CH_3	180	79	60

TABLE 2



Sl. No.	Nature of R	Nature of R'	Nature of R''	M.P. °C	% Germination inhibition at 1000 ppm conc. *P. oryzae*	*H. oryzae*
1	2	3	4	5	6	7
17.	C_6H_5	C_6H_5	CH_3	184	100	100
18.	C_6H_5	H	CH_3	188	89	67
19.	C_6H_5	$CONH_2$	CH_3	179	68	60
20.	C_6H_5	C_6H_5	C_6H_5	186	100	62
21.	H	C_6H_5	CH_3	210	88	67
22.	H	H	CH_3	above 350	79	60
23.	H	$CONH_2$	CH_3	above 350	89	74
24.	H	C_6H_5	C_6H_5	197	100	60

TABLE 3



Sl. No.	Nature of R	Nature of R'	Nature of R''	M.P. °C	% Germination inhibition at 1000 ppm conc. *P. oryzae*	*H. oryzae*
1.	2	3	4	5	6	7
25.	C_6H_5	C_6H_5	CH_3	230	72	56
26.	C_6H_5	H	CH_3	199	45	40

(Table 3 Contd.)

27.	C_6H_5	$C_6H_4NO_2$(p-)	C_6H_5	160	64	60
28.	C_6H_5	H	C_6H_5	202	64	52
29.	C_6H_5	$C_6H_3(NO_2)_2$(2,4-)	C_6H_5	144	60	49
30.	C_6H_5	$C_6H_3(NO_2)_2$(2,4-)	CH_3	148	60	46
31.	C_6H_5	$CONH_2$	CH_3	226	52	46
32.	C_6H_5	$C_6H_3(NH_2)_2$(2,4)-	CH_3	196	60	54
33.	H	H	CH_3	225	78	55
34.	H	C_6H_5	CH_3	199	45	40
35.	H	$C_6H_4NO_2$(p-)	C_6H_5	186	61	50
36.	H	$C_6H_3(NO_2)_2$(2,4-)	C_6H_5	195	68	54

It was noted that compounds (1-6, 8-10, 13, 14, 17, 18, 20, 21, 23, 24) inhibited spore germination in the same range as the standard fungicides like *o*-Ethyl-S, S-diphenyl phosphoro dithioate (Hinosan 50%) EC, Difolatan 50% WP and Derosal 60% WP; thus these may prove as promising fungicides. In conclusion, it is found that introduction of a C_4-nitroso group enhances the fungicidal activity whilst the activity considerably decreases when a $C_4=C_{4'}$ double bond is introduced into the *bis*-derivatives.

Experimental

4, 4'-Bis-(1-phenyl-3-methyl-2-pyrazolin-5-one) :

1-Phenyl-3-methyl-2-pyrazolin-5-one (1 g), 1-phenyl-3-methyl-4-bromo-2-pyrazolin-5-one (1 g) and fused sodium acetate (1 g) were taken in ethanol (5 ml). The resulting mixture was refluxed over a water bath for 2 hrs. The alcohol was then boiled off and distilled water (10 ml) was added. It was allowed to stand for 2 hrs. A white compound separated out which was filtered and dried. On crystallisation from ethanol, it yielded white coloured crystals, m.p. 320°(d), yield 80%.

The compound is soluble in 10% aqueous sodium hydroxide and gives colouration with alcoholic ferric chloride.

ν_{max}^{KBr} 1595, 1500 cm^{-1}.

1-Phenyl-3-methyl-2-pyrazolin-4-(1'-phenyl-3'-methyl-4'-nitroso-2'-pyrazolin-5'-one-4'-yl)-5-one :

1-Phenyl-3-methyl-4-nitroso-2-pyrazolin-5-one (1 g) was taken along with 1-phenyl-3-methyl-4-bromo-2-pyrazolin-5-one (1.2 g) and fused sodium acetate (1 g) in ethanol (5 ml). The resulting mixture was refluxed over a water bath for 2 hrs. The alcohol was then boiled off and distilled water (10 ml) was added to it. The whole solution was allowed to stand for 2 hrs. A yellowish brown coloured compound was obtained. On crystallisation from ethanol, it yielded yellowish brown crystals, m.p. 184°, yield 80%.

The compound is soluble in 10% aqueous sodium hydroxide and gives colouration with alcoholic ferric chloride.

ν_{max}^{KBr} 1715, 1590, 1540 cm^{-1}.

$C_{4,4'}$ unsaturated product of 4, 4'-bis-(1-phenyl-3-methyl-2-pyrazolin-5-one) :

To 4, 4'-*bis*-(1-phenyl-3-methyl-2-pyrazolin-5-one) (1 g) was added (1 : 1) HNO_3 (5 ml). Immediately a blue pasty mass was produced which was converted into blue solid after a few minutes. The compound was filtered, washed with 10% sodium hydroxide and dried. On crystallisation from acetone, it produced blue crystals, m.p. 230°, yield 80%.

The same compound was also obtained by using iodine in potassium iodide[10].

The compound is soluble in 10% aqueous sodium hydroxide and gives no colouration with alcoholic ferric chloride.

ν_{max}^{KBr} 1695, 1590, 1280, 980 cm^{-1}.

λ_{max}^{EtOH} 206^{nm} <(log t = 4.6749),

246^{nm} <(log t = 4.5794)

NMR (CCl_4) : δ 2.03(S, 3*H*), 2.43(S, 3*H*),

The fungicidal data of the synthesised compounds are listed in Tables 1, 2 and 3. The compounds (1, 9, 25, 33) are already reported in literature. All compounds showed satisfactory elemental analyses.

Acknowledgement

The authors are thankful to the Director, Central Rice Research Institute, Cuttack for providing necessary facilities to carry out the fungicidal tests.

References

1. B. NANDA, S. PADMANAVAN, B. TRIPATHY and A. S. MITTRA, *J. Indian Chem. Soc.*, 1975, **52**, 533.
2. A. NAYAK, S. DAS, C. R. MISHRA and A. S. MITTRA, *J. Indian Chem. Soc.*, 1977, **54**, 485.
3. S. RAO and A. S. MITTRA, *Indian J. Chem.*, 1977, **15B**, 1062.
4. S. K. MOHANTY, R. SRIDHAR, S. RAO, S. Y. PADMANAVAN and A. S. MITTRA, *Indian J. Chem.*, 1977, **15B**, 1146.
5. N. B. DAS and A. S. MITTRA, *Indian J. Chem.*, (In press).
6. N. B. DAS and A. S. MITTRA, *Indian J. Chem.*, (Communicated).
7. A. NAYAK, B. NANDA and A. S. MITTRA, *Indian J. Chem.*, (Communicated).
8. A. NAYAK and A. S. MITTRA, *J. Indian Chem. Soc.*, 1978, **55**, 593.
9. S. C. DE and N. C. DUTTA, *J. Indian Chem. Soc.*, 1926, **3**, 30.
10. L. KNORR, *Ann.*, 1887, **137**, 283.
11. A. MOORE and J. MONTGOMERY, *J. Promol. Hort. Sci.*, 1938, **15**, 253.

NOTES

Magneto-electrophoretic Study of Ions on Filter Paper

(Comparative study of some ligand fields)

H. G. MUKHERJEE* and D. MAJUMDAR

Pure Chemistry Department, Calcutta University, India

Manuscript received 14 February 1980, accepted 13 May 1980

IN the present work[1], an attempt is made to compare qualitatively the field strength of some common ligands. It is known that some ligands like CN^- give rise to weakly paramagnetic complexes even when the central metal ion is strongly paramagnetic. For example, Fe^{3+} is strongly paramagnetic as free ion but the complex $K_3[Fe(CN)_6]$ is weakly paramagnetic. But the same ion is found to form strongly paramagnetic complex $K_3[FeF_6]$ with F^- as ligand. Hence the behaviour of ligands are different in respect of the magnetic susceptibility of the complexes formed by them. In text books, this property of ligands has been explained in terms of the "ligand field strength" or the "spin-pairing capacity" of the ligand. In the present work the field-strengths of some more common ligands are qualitatively compared.

Apparatus and Chemicals :

An electromagnet of 15 kilogauss strength, an ammeter, a milliammeter, a voltmeter, two rheostats, platinum electrodes, thin glass plates, beakers, switches, etc.

Filter paper used for the purpose of electrophoresis was Whatman No. 1 grade. Along with other chemicals, reagent quality oxalic acid, disodium salt of EDTA, potassium cyanide, potassium chloride, Mohr's salt, hydrofluoric acid, potassium ferrocyanide, potassium ferricyanide, etc, were used.

Experimental

The circuit is made as shown in the diagram. The electromagnet is connected in series with a switch, an ammeter, a rheostat ; and a voltmeter is connected in parallel to this. The electrophoresis set is run through a different circuit and the milliammeter and the rheostat are connected in series. In a previous experiment, the field strength of the magnet was calibrated against the current flowing and thus the field strength is known at the time of experiment from the ammeter reading only. The field strength is made as desired by controlling the current through the ammeter with the help of the rheostat.

The electrophoresis set is run by a separate switch and the current flowing through the paper can be controlled by the rheostat. The current can be read on the milli-ammeter.

Whatman No. 1 filter paper is cut into 1 cm × 40 cm strips. In a single observation a single strip is used. The complex to be studied is spotted (.01 ml) on a marked zero-line on the strip in the form of a normal solution. The strip is then moistened with the carrier electrolyte (M/5 KCl) solution. The strip is then sandwiched between the thin glass plates and the zero-line of the strip (visible through the glass plate) is placed at the centre of the magnetic field. The ends of the strip are dipped into the beakers full of the electrolyte and provided with platinum electrodes which form the cells. After the run the strip is dried in air oven and then developed with a suitable reagent.

Some of the complexes, e.g., $K_4[Fe(CN)_6]$, $K_3[Fe(CN)_6]$ are available in reagent quality samples. The rest are prepared in the laboratory from reagent quality starting materials using standard methods of synthesis.

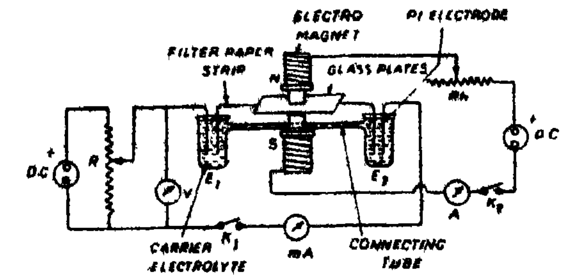
EXPERIMENTAL DATA :

Carrier electrolyte : M/5 KCl solution,
Time of migration : 15 minutes
Terminal voltage : 220 volt D.C.
Maximum field strength : 15 kilogauss at 1.4 amp.
Half field strength : 7.5 kilogauss at 0.6 amp.

Central metal ion	Ligand	Complex in	Distance of the central line in mm from origin: without field	with half field	with full field
Mn^{2+}	CN^-	$[Mn(CN)_6]^{4-}$	25	19	16
	EDTA	$[Mn\text{-}EDTA]^{2-}$	22	18	13
	$C_2O_4^{2-}$	$[Mn(C_2O_4)_3]^{4-}$	20	17	12
Fe^{3+}	CN^-	$[Fe(CN)_6]^{3-}$	25	19	15
	EDTA	$[Fe(EDTA)]^-$	22	16	13
	$C_2O_4^{2-}$	$[Fe(C_2O_4)_3]^{3-}$	22	14	9
	F^-	$[FeF_6]^{3-}$	32	18	12
Co^{3+}	CN^-	$[Co(CN)_6]^{3-}$	22	18	15
	EDTA	$[Co\text{-}EDTA]^-$	22	17	12
	$C_2O_4^{2-}$	$[Co(C_2O_4)_3]^{3-}$	23	17	12
	F^-	$[CoF_6]^{3-}$	28	20	14

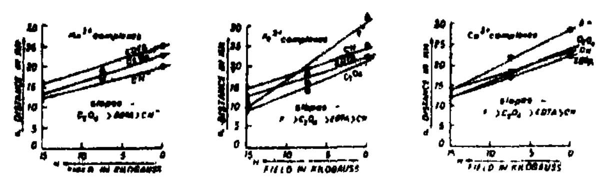
* For correspondence.

Circuit Diagram :



Discussion

In the above experiment, it is clear that the ligands are different in their capacity of "spin pairing" or producing low-spin complexes from high spin central metal ions. The central atoms Mn^{2+} (5 unpaired electrons, d^5), Fe^{3+} (5 unpaired electrons, d^5) and Co^{3+} (4 unpaired electrons d^6) are all highly paramagnetic ions. But the results of magnetoelectrophoresis show that all their cyano-complexes are weakly paramagnetic. Thus CN^- is a very strong-field ligand. On the other hand, the fluoro-complexes are highly para magnetic. Hence F^- is a weak field ligand. From the nature of the curves obtained++ by plotting the data from the Table, it is possible to write the ligands with respect to their ligand-field strength, the following sequence·:



Low Ligand Field High

F^- $C_2O_4^=$ EDTA CN^-

In the graph, distance migrated is plotted against field strength, from the slope of the curve, the paramagnetism of the complex is indicated, i.e., greater the slope, more is the paramagnetism, i.e., less is the ligand field. So, the order of the ligand field will be the reverse of the slope.

Reference

1. H. G. MUKHERJEE and D. MAJUMDAR, *Z. Anal. Chem.*, 1976, 277, 206.

Addition Complexes of Cobalt(II) and Nickel(II) Haloacetates with Nitrogen Donors

N. KUMAR and A. K. GANDOTRA

Department of Chemistry, University of Jammu, Jammu 180 001, India

Manuscript received 6 June 1978, revised 16 July 1979, accepted 19 May 1980

THIS is in continuation to our work on complexes of cobalt(II) and nickel(II) carboxylates with pyridine type bases[1-3] and we wish to report now preparation and characterisation of a number of complexes of cobalt(II) and nickel(II) haloacetates with heterocyclic ligands pyridine (Py), 2-, 3- and 4-methylpyridine (2-, 3-, 4-MePy), quinoline(Q) and isoquinoline(IQ) with a view to investigate their structure.

Experimental

Cobalt(II) and nickel(II) haloacetates were generated in solution by the interaction of the appropriate haloacetic acid with an excess of the required basic metal carbonate in ethanol under reflux and filtering off the excess of the unreacted metal carbonate. However, dichloroacetates of cobalt(II) and nickel(II) were isolated as solid samples by concentration of the filtrate obtained as described above. The initial crude products were *recrystallised from methanol and dried in vacuum* over phosphorus pentoxide. Their purity was established by metal analysis. Heterocyclic ligands were purified by fractional distillation over potassium hydroxide before use.

Preparation of Complexes : Complexes of mono- and trihaloacetates were prepared by the direct addition of the ligand in 1 : 2 molar ratio to the appropriate metal(II) haloacetate generated in ethanol. The reaction mixture on concentration and crystallisation invariably gave a solid crystalline product which was separated, washed with the appropriate solvent and dried in vacuum over phosphorous pentoxide.

Complexes of cobalt(II) and nickel(II) dichloroacetates were prepared by mixing the reactants in 1 : 2 or 1 : 4 metal to ligand ratios in acetone medium and working up the reaction mixture as described above.

Cobalt and nickel were estimated gravimetrically as tetrapyridinedithiocynatocobalt(II) and *bis*(dimethylglyoximato)-nickel(II) respectively. Carbon and hydrogen contents of the samples were estimated in the micro-analytical laboratory of this department. Conductance measurements were carried on millimolar solutions in acetone using a Toshniwal Conductivity Bridge type CL 01/0,2A. Molecular weights were determined cryoscopically in nitrobenzene. Magnetic moments were determined by Gouy's method. Electronic spectra were recorded in chloroform on Beckman-DB-Spectrophotometer over the range 28,500-12,500 cm^{-1}. Infrared spectra were recorded in Nujol mulls on a Perkin-Elmer Infrared Spectrophotometer Model 621.

The analytical results, magnetic moments, conductivity and molecular weights wherever recorded are cited in Table 1.

Results and Discussion

Analytical results show that the complexes formed are either of 1 : 2 or 1 : 4 stoichiometry.

TABLE 1—MAGNETIC, CONDUCTANCE, ANALYTICAL AND MOLECULAR WEIGHT DATA OF THE COMPLEXES

Sl. No.	Compound	Colour	μ_{eff} B.M.	Conductance mole^{-1} ohm^{-1} cm^{2}	Metal(%) Found	Metal(%) Calcd.	Carbon(%) Found	Carbon(%) Calcd.	Hydrogen(%) Found	Hydrogen(%) Calcd.	Molecular weight Found	Molecular weight Calcd.
1.	$Co(O_2CCH_2Cl)_2(3\text{-}MePy)_2$	Pink	5.02	4.32	13.76	13.95	44.34	44.48	4.03	4.15		
2.	$Co(O_2CCH_2Cl)_2(Q)_2$	Pink	4.95	4.74	11.57	11.74	52.08	52.36	3.32	3.56		
3.	$Co(O_2CCHCl_2)_2(3\text{-}MePy)_2$	Pink	5.07	4.92	11.86	11.76	38.12	38.32	3.31	3.19	578	501
4.	$Co(O_2CCHCl_2)_2(4\text{-}MePy)_2$	Pink	5.05	5.05	11.45	11.76	38.18	38.32	3.12	3.19		
5.	$Co(O_2CCHCl_2)_2(IQ)_2$	Pink	5.05	4.92	10.18	10.28	45.35	46.39	2.70	2.82	580	578
6.	$Co(O_2CCHCl_2)_2(3\text{-}MePy)_4$	Red	5.02	4.34	8.34	8.57	49.00	48.87	3.95	4.35	508	687
7.	$Co(O_2CCHCl_2)_2(4\text{-}MePy)_4$	Red	4.96	5.98	8.49	8.57	48.34	48.87	4.07	4.35		
8.	$Co(O_2CCHCl_2)_2(IQ)_4$	Red	4.95	4.87	7.01	7.09	58.00	57.74	3.45	3.61	602	831
9.	$Co(O_2CCCl_3)_2(4\text{-}MePy)_2$	Pink	5.03	10.82	10.21	10.34	33.51	33.70	2.16	2.45		
10.	$Co(O_2CCF_3)_2(IQ)_2$	Pink	4.96	17.32	10.58	10.87	—	48.73	—	2.58		
11.	$Ni(O_2CCH_2Cl)_2(Py)_2$	Light blue	3.15	4.52	14.27	14.53	41.42	41.59	3.22	3.45		
12.	$Ni(O_2CCHCl_2)_2(3\text{-}MePy)_2$	Light blue	3.19	5.08	11.55	11.70	38.21	38.34	3.20	3.19		
13.	$Ni(O_2CCHCl_2)_2(4\text{-}Mepy)_2$	Light blue	3.16	7.27	11.52	11.70	38.18	38.34	3.07	3.19	464	501
14.	$Ni(O_2CCHCl_2)_2(IQ)_2$	Light blue	3.20	8.78	10.02	10.26	46.25	46.42	2.66	2.81	591	642
15.	$Ni(O_2CCHCl_2)_2(3\text{-}MePy)_4$	Blue	3.16	4.32	8.36	8.55	48.71	48.88	4.23	4.35		
16.	$Ni(O_2CCHCl_2)_2(4\text{-}MePy)_4$	Blue	3.20	5.85	8.28	8.55	48.68	48.88	4.27	4.35	527	687
17.	$Ni(O_2CCHCl_2)_2(IQ)_4$	Blue	3.20	7.04	6.98	7.07	57.'8	57.76	3.38	3.61	598	831
18.	$Ni(O_2CCCl_3)_2(4\text{-}MePy)_2$	Light blue	3.20	12.78	10.15	10.30	33.58	33.72	2.31	2.45		
19.	$Ni(O_2CCF_3)_2(IQ)_2$	Light blue	3.22	18.52	10.68	10.75	—	48.78	—	2.58		

1 : 2 complexes are formed by all the metal(II) haloacetates but 1 : 4 complexes are formed by dichloroacetates of cobalt(II) and nickel(II) only. All the complexes are coloured and dissolve in common organic solvents giving stable solutions except those of 1 : 4 complexes which break up in solution to corresponding 1 : 2 complexes. Their conductance values (Table 1) indicate that complexes are non ionic[4]. Molecular weight studies on *bis*-amine complexes show them to be monomeric in solution. Magnetic moments of cobalt(II) and nickel(II) complexes fall in the range of 4.95-5.07 and 3.15-3.22 B. M. respectively suggesting that the complexes are of high-spin octahedral configuration.

In their electronic spectra cobalt complexes show a strong band around 19,500 cm^{-1} along with a shoulder around 20,500 cm^{-1}. The strong band like various other octahedral cobalt(II) complexes is assigned to $^4T_{1g} \rightarrow {}^4T_{1g}$ (P) transition and the shoulder may be observed to arise from the splitting of the visible band on account of spin-orbit coupling and/or the presence of quartet-doublet transitions[5]. The low value of molar extinction coefficient (*Ca*.30 l. mole^{-1} cm^{-1}) of these complexes further suggest that they have a transoctahedral configuration[6]. Complexes of nickel(II) carboxylates show two bands of low intensity (ϵ 10 l. mole^{-1} cm^{-1}) in the regions 15,740-15,900 and 26,000-27,300 cm^{-1} and are assigned to $^3A_{2g} \rightarrow {}^3T_{1g}$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions respectively pointing octahedral disposition of the complexes[5].

Infrared spectra of all the complexes show a positive shift in almost all the frequencies originating from the ligand suggesting that the pyridine ligand coordinates through its nitrogen atom[7]. The frequency difference, Δ, between the asymmetric and symmetric stretching frequencies of the carboxylate group in the 1 : 2 complexes of metal(II) mono, di, tri-chloro and trifluoroacetates lie in the range 250-255, 280-295, 335-350 and 315-325 cm^{-1} respectively which are in close agreement to the Δ values observed in corresponding *bis*-amine complexes of cobalt(II) and nickel(II) haloacetates with pyridine[3] indicating that the complexes are octahedral and haloacetate group is coordinated as a bidentate chelating ligand. This is further supported by C – F stretching frequencies which appear at 1200 and 1130 cm^{-1} in cobalt trifluoroacetate complex and at 1170 and 1125 cm^{-1} in nickel trifluoroacetate complex[6]. In 1 : 4 complexes Δ values lie in the range of 315-325 cm^{-1} which show that the complexes under study are octahedral in which dichloroacetate group functions as a monodentate ligand[6].

Acknowledgement

The authors are thankful to Professor O. P. Vig, Head, Department of Chemistry, Panjab University, Chandigarh for providing facilities to carry out physical studies on these complexes.

References

1. B. S. MANHAS, G. S. JOLLY, N. KUMAR and A. K. GANDOTRA, *J. Chem. Sci.*, 1975, **1**, 1; *Chem. Abs.*, 1976, **85**, 153240h.
2. N. KUMAR and A. K. GANDOTRA, *Acta Ciencia, Indica*, 1977, **3**, 198.
3. N. KUMAR and A. K. GANDOTRA, *J. Indian Chem. Soc.*, 1978, **55**, 535.
4. R. S. NYHOLM, R. G. CUNNINGHAME and M. L. TOBE, *J. Chem Soc. Dalton*, 1972, 229.
5. A B. P. LEVER, 'Inorganic Electronic Spectroscopy'', Elsevier, Amsterdam, 1968.
6. F. A. COTTON, D. M. GOODGAME and R.H. SODERBERG, *Inorg. Chem.*, 1963, **2**, 1162.
7. N. N. GREENWOOD and K. WADE, *J. Chem. Soc.*, 1960, 1130.

8. A. B. P. Lever and D. Ogden, *J. Chem. Soc. (A)*, 1967, 2041.

9. C. A. Agambar, P. Anastassy and K. G. Orrell, *J. Chem. Soc. Dalton*, 1974, 964.

Studies in Fe(III) 6, 7-Dihydroxy-Naphthalene-2-Sulphonic Acid Complexes

M. L. NARWADE, S. W. SATHE and M. V. KARBELKAR

Department of Chemistry, Vidarbha Mahavidyalaya, Amaravati

Manuscript received 8 November 1977, revised 24 April 1979, accepted 19 May 1980

SULPHONIC acids are known to form coloured *complexes with Fe(III). Mc.Bryde' has studied* Fe(III)complexes of 8-hydroxyquinoline-7-sulphonic acid spectrophotometrically. Recently Narwade[2] has investigated the interaction of transitional metal ions with sulphonic acids.

A preliminary experiment with solutions containing Fe(III) perchlorate ($1 \times 10^{-1} M$) and sodium salt of 6-7 dihydroxy-naphthalene-2-sulphonic acid (6, 7 DHN-2SA), ($20 \times 10^{-2} M$) and free $HClO_4$ showed colour change from dark-blue, violet and then to orange when pH was varied from 2 to 8. This indicated the presence of more than one complex species in solution. A potentiometric study was undertaken to determine the stability constants of complexes of Fe(III) with 6, 7 DHN-2SA. Spectrophotometric study was made with a limited aim to confirm the result of potentiometry.

Experimental

Potentiometry : The experimental procedure involved the Calvin-Bjerrum titrations of three carbonate-free mixtures : (1) Free $HClO_4$ ($1.002 \times 10^{-2} M$), (2) Free $HClO_4$ (1.002×10^{-2})+6, 7 DHN-2SA ($20.0 \times 10^{-4} M$) and (3) Free $HClO_4$ ($1.002 \times 10^{-2} M$)+6, 7 DHN-2SA+Ferric perchlorate ($4.0 \times 10^{-4} M$). All the mixtures were titrated separately with 0.1818*M* NaOH solution in a double walled titration vessel with a seal on water jacket at a temperature of 25°±0.2°. Total volume was 50 ml each time. The ionic strength of 0.1*M* was main*tained constant by adding* $NaClO_4$ *solution.* The titrations were carried out in an inert atmosphere by bubbling oxygen free nitrogen gas through the assembly containing the electrodes in order to exclude CO_2.

pH measurements were made with a ELICO pH Meter (accuracy±0.05 unit) using glass and calomel electrodes.

From the shifts in the pH titration curves the values of $\bar{n}$A, $\bar{n}$ and pL, were calculated by Irving and Rossotti's method.

Results and Discussion

The acid+ligand curve was found to be coinciding with the acid curve upto pH 6.0 (Fig. 1). This was expected as the ligand 6, 7 DHN-2SA was taken in the form of its sodium salt. In water, the salt dissociates into sodium ion and ionic ligand (H_2L^-). The sulphonic acid is a good chelating agent and is highly acidic due to its $-SO_3H$ group. The dissociation equilibria can be represented as under :

$$H_2L^- \overset{K_1}{\rightleftharpoons} HL^{2-} + H^+ \text{ and } HL^{2-} \overset{K_2}{\rightleftharpoons} L^{3-} + H^+$$

From the plot of $\bar{n}_A$ vs pH (Fig. 1a) pK values were determined. The pK_1 (first dissociation constant *of* $-OH$ *group) at* $\bar{n}_A = 1.5$, *which was found 8.10,* be ascribed to the $-OH$ group in the 6th position,

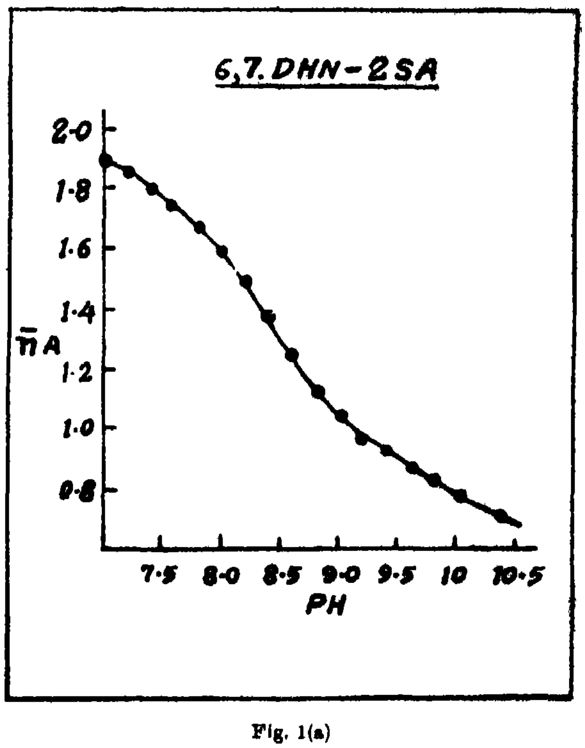


Fig. 1(a)

because the overall electron withdrawing effect of the $-SO_3^-$ group is efficiently transferred to the 6-hydroxy group. The hydrogen bonding between the pentoxide ion of 6th position and the $-OH$ group at the 7th position would increase the dissociation constant of the $-OH$ group in 7th position leading to a higher value of pK_2 (second dissociation constant of $-OH$ group). The accurate pK_2 value could not be determined due to the limited accuracy of glass electrode above pH 11.0. Actual titrations are carried out above pH 12.0. The value of pK_2 corresponding to the pH, where $\bar{n}_A = 0.5$

could not be found by this method. The value of pK_2 for $-OH$ group was calculated by the expression—

$$2pH = pK_1 + pK_2 \text{ and from the } \bar{n}_A = 1$$

Knowledge of pK_1 : The value of pK_2 was found out to be 10.4. Kabadi *et al*[4] have determined the values of pK_2 of salicylaldehyde and salicylic acid by using above expression.

The deviation of (acid + ligand + metal ion) curve from the (free acid + ligand) curve was observed from pH 2.0. Precipitation was not observed upto pH 9.0. This observation together with the fact that concentrations employed were low, excluded factors like hydrolysis of Fe(III) and presence of polynuclear hydrogen and hydroxyl bearing complexes. This faciliteted the calculation of stability constants of the complexes. The colour of solution was dark blue upto pH 3.0, orange above pH 7.0 and violet in the intermediate pH range. The departure of metal complex titration curve from the reagent (ligand) titration curve was observed at pH less than 2.0. This clearly indicated that Fe(III) forms 1 : 1 complex below pH 2.0. The maximum value of $\bar{n}$

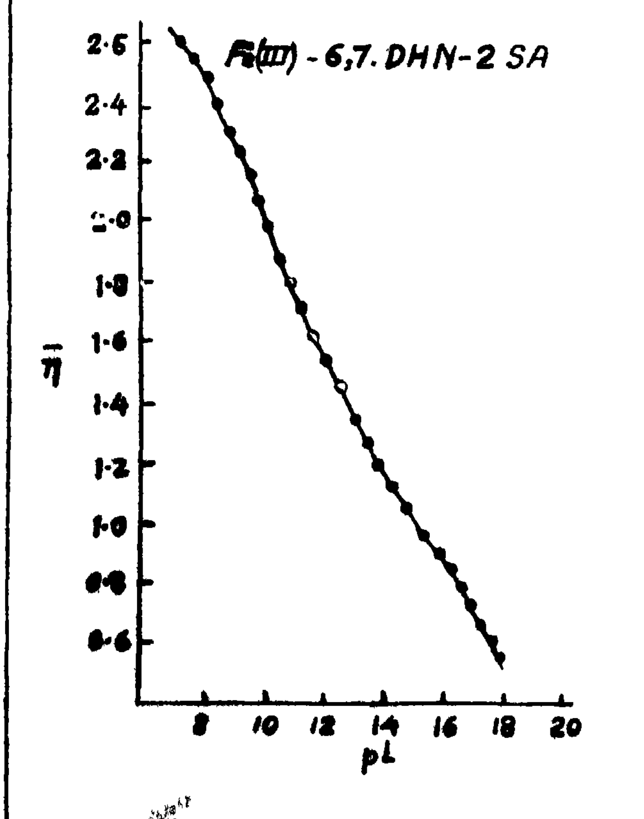


Fig. 1(b)

was found to be 2.9 indicating the presence of 1 : 1, 1 : 2 and 1 : 3 complex formations in solution. The values of pL at $\bar{n}$ 0.5, 1.5, 2.5 [Fig. 1(b)]were utilised to calculate the metal-ligand stability constants. The values of log K_1, log K_2 and log K_3 were found 18.10, 12.40, 8.00 respectively. The reported[3] values of log K_1 and log K_2 of Cu(II) and Ni(II) complexes with 6, 7 DHN-2SA are 13.01 and 10.73; and 10.52 and 6.23 respectively. The sulphonic acid complexes of Fe(III) ion are more stable than Cu(II) and Ni(II), because Fe(III) is expected to be a hard acid.

Spectrophotometry :

For confirming the formation of complexes of Fe(III) with 6, 7 DHN-2SA, the method due to Varielle[4] was employed. Various solutions of metal ion and ligand in the ratio of 1 : 20 were prepared in the pH range of 2.0 to 8.0. The ionic strength of each solution was maintained at 0.1M by adding $NaClO_4$ solution. The spectra were recorded by AIMIL Spectrochem(PEI). The curves were constructed by plotting optical density of complex against wavelength in nm (Fig. 2). The curves were

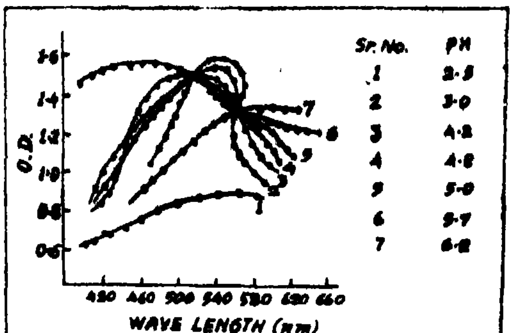


FIG. 2

found to intersect at two isobestic points corresponding to wavelength of 520 nm and 56 nm respectively. This existence of the two isobestic points indicated the presence of three different complex species in the pH range of 2.0 to 8.0. The curve below pH 2.5 did not pass through any of the isobestic points. It could be concluded that below pH 2.5 the solution contained exclusive 1 : 1 complex.

Acknowledgement

Our sincere thanks are due to Principal, Vidarbha Mahavidyalaya, Amaravati for providing all facilities.

References

1. W. A. E. Mc. Bryde, *Canad. J. Chem.*, 1964, 42, 1917.
2. M. L. Narwade, Ph. D. Thesis, Marathwada University, Aurangabad, Oct., 1974.
3. H. Irving and H. S. Rossotti, *J. Chem. Soc.*, 1953, 3397.

4. L. Varibelle, *Bull. Soc. Chim. Fr.*, 1955, 870.
5. M. B. Kabadi, K. B. Jabalpurwala and K. A. Venkatachalam, *J. Inorg. Nuclear Chem.* 1964, 26, 1011.

Thermodynamic Studies of Cr(II), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) Chelates of o-(N-α-furfuralideneimino) Benzene Sulphonic Acid

C. P. GUPTA, N. K. SANKHLA, K. G. SHARMA
and
R. K. MEHTA

Department of Chemistry, University of Jodhpur, Jodhpur (India)

Manuscript received 21 August 1978, revised 4 March 1980, accepted 13 May 1980

A perusal of the literature[1-3] shows that no systematic study has been made on the bivalent metal chelates of *o*-(N-α-furfuralideneimino) benzene sulphonic acid (HFB), hence the same was undertaken. The findings of these studies are reported in the present paper.

Experimental

Metal salt used were of BDH AnalaR quality. Furfuraldehyde and orthanilic acid (L. R.) supplied by Fluka were used. Precision *p*H-meter type OP : 205 No. 837 (Radelkis) equipped with a glass-calomel electrode assembly was used at 25°, 35° and 45° (μ=0.01, 0.05 and 0.1*M* $NaClO_4$). HFB was synthesised from furfuraldehyde and orthanilic acid by the method reported earlier[3]. It gave satisfactory elemental analyses. The titrations were carried out in presence and in absence of the metal ions, against carbonate free 0.01*M* NaOH in accordance with Calvin's extension of Bjerrum method[4,5].

Results and Discussion

From the titration curves it is observed that the metal-ligand curve is well separated from the ligand titration curve which suggests that liberation of proton occurs due to complexation. The *p*K, of HFB as determined by interpolation at half $\bar{n}$ values and algebraic method[6] was 5.95, 5.77 and 5.60 at 25°, 35° and 45°. Thus the *p*K values fall with rise of temperature. These values suggest that HFB is a monoprotic ligand. The metal-ligand stability constants were read from the formation curves drawn by plotting $\bar{n}$ vs $-\log[A^-]$. The refinement was done by various computational method[7], such as correction term, convergence formula successive approximation and interpolation at various $\bar{n}$ values methods and their average value (log β_2) along with their deviations from the theoretical values are summarised in Table 1. The log β_2 values of the metal chelates are in the order Cu(II)>Ni(II)>Co(II)>Fe(II)>Mn(II)>Cr(II) which is in accordance with the Irving-William rule[8].

The thermodynamic stability constants (log K°) as shown in Table 1 have been obtained by extrapolation of measured formation constants to zero ionic strength from graph between log of stability constant vs $\sqrt{\mu}$, where μ is the ionic strength.

The values of overall changes in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) have been evaluated using Gibbs-Helmholtz equation[6], (Table 1). The ΔG of all the chelates have more

TABLE 1—AVERAGE STABILITY CONSTANTS, THEIR DEVIATIONS* FROM THEORETICAL VALUES AND THERMODYNAMIC FUNCTIONS OF THE BIVALENT METAL CHELATES OF *o*-(N-α-FURFURALIDENEIMINO) BENZENE SULPHONIC ACID AT 25°, 35° AND 45°

Metal		Stability constant (μ=0.1*M* $NaClO_4$) 25°	35°	45°	log K° 25°	35°	45°	−ΔG K cal/mole 25°	35°	45°	ΔH K cal/mole 35°	ΔS cal/deg/mole at 35°
Cr(II)	log K_1	3.68	3.75	3.78	7.00	7.20	7.40	9.03	9.40	10.08	15.18	80.28
	log K_2	2.70	2.82	2.95								
	log β_2	6.38±0.02	6.57±0.05	6.73±0.08								
Mn(II)	log K_1	3.86	3.96	4.06	8.25	8.60	8.70	9.49	10.26	10.94	14.09	78.89
	log K_2	3.02	3.24	3.47								
	log β_2	6.88±0.04	7.20±0.02	7.53±0.01								
Fe(II)	log K_1	3.96	4.05	4.15	8.45	8.75	9.00	9.82	10.50	11.19	12.80	74.01
	log K_2	3.16	3.35	3.54								
	log β_2	7.12±0.03	7.40±0.04	7.69±0.04								
Co(II)	log K_1	4.23	4.37	4.66	9.05	9.35	9.70	10.59	11.45	12.32	17.13	92.76
	log K_2	3.45	3.63	3.81								
	log β_2	7.68±0.02	8.00±0.04	8.47±0.02								
Ni(II)	log K_1	4.41	4.51	4.61	9.30	9.65	9.95	11.28	12.08	12.89	14.74	87.06
	log K_2	3.77	4.01	4.25								
	log β_2	8.18±0.05	8.52±0.02	8.86±0.01								
Cu(II)	log K_1	4.80	4.86	4.92	10.00	10.20	10.50	12.28	13.08	13.81	21.67	112.7
	log K_2	4.19	4.35	4.57								
	log β_2	8.99±0.03	9.21±0.01	9.49±0.04								

* Very small deviations (0.01-0.05) were observed.

negative values at 45° than at 25° or 35°. It is also observed that ΔH is positive in all cases which suggests that there exists steric strain around the metal ion in the chelates due to fused rings. The positive values of ΔS for all the chelates indicate that entropy term is favourable for their formation.

The data were analysed in terms of Harned's[10] relation between log $K^{\neq}$ and temperature $[(pK^{\neq} - ct^2) = -2c\theta t + (pK^{\neq}_m - c\theta^2)]$. A plot of $(pK^{\neq} - ct^2)$ vs t must be linear and this was found true in the present case. The values of $\theta°$ and $pK^{\neq}_m$ for HFB were found 211° and 3.550 respectively. ΔH values as calculated from Harned's equation were found 7.914, 7.794 and 7.681 at 25°, 35° and 45° respectively.

Acknowledgement

The authors are thankful to UGC (India) for the award of fellowships to two of them (NKS & CPG).

References

1. F. A. COTTON, *Prog. Inorg. Chem.*, 1966, **7**, 88.
2. D. J. HODGSON, *Prog. Inorg. Chem.*, 1975, **19**, 1.
3. R. K. MEHTA and R. K. GUPTA, *Indian J. Chem.*, 1973, **11**, 56.
4. M. CALVIN and K. W. WILSON, *J. Amer. Chem. Soc.*, 1945, **67**, 2003.
5. J. BJERRUM, Metal Ammine Formation in Aqueous Solution P. Hasse & Sons, Copenhagen, 1941.
6. J. BJERRUM, Metal Ammine Formation in Aqueous Solution P. Hasse and Sons, Copenhagen, 1957, 114, p. 20, 14(a), 36(b)
7. H. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.*, 1953, 3397.
8. H. IRVING and R. J. P. WILLIAM, *Nature*, 1948, **162**, 746.
9. YATSIMIRSKII and V. P. VASILEV, Instability Constant of Complexes Compound (D. Van Nostrand, New York).
10. H. S. HARNED and R. W. EHLERA, *J. Amer. Chem. Soc.*, 1933, **55**, 652.

Separation and Determination of Zirconium with N-Benzoyl-*o*-Tolyl Hydroxylamine

A. K. MAJUMDAR, A. K. CHAKRABURTTY

and

RUHIDAS SAHA

Department of Chemistry, Jadavpur University, Calcutta-700 032

Manuscript received 5 July 1979, revised 29 March 1980, accepted 13 May 1980

N-BENZOYL-*O*-TOLYL hydroxylamine which was used for the precipitation and determination of niobium and tantalum by Majumdar and Pal[1] has later been used as a reagent in gravimetric and spectrophotometric determination of a variety of metals[2-3].

Experimental

Reagent :

N-benzoyl-*o*-tolyl hydroxylamine was prepared by the procedure given by Pal[4]. The product was recrystallised from ethanol.

Standard Solution :

A standard solution of zirconium was prepared from Johnson & Mathey 'Specpure' zirconium oxychloride. The solution of zirconium was standardised gravimetrically as oxide by cupferron[5] and N-benzoyl phenyl hydroxylamine[6-7].

An Elico Model L 1-10 pH – meter was used for all pH measurements.

Procedure :

An aliquot of standard zirconium solution was diluted to 100 ml, pH was adjusted between 0.4-2.2 with dilute ammonia or mineral acid and the solution warmed. The reagent in ethanol and water mixture (1 : 1) was then added to the solution very slowly with thorough stirring after each addition, when a milky white precipitate appeared, which was digested for 20-25 minutes on the boiling water bath. The solution was then cooled to room temperature and filtered through a Whatman No. 42 filter paper, washed with 0.1% reagent solution and ignited to oxide in a platinum crucible.

pH effect :

The precipitate of zirconium was found to be quantitative between pH 0.4 to 2.2 ; at higher pH zirconium precipitate assumed colloidal form and at higher acid concentrations the precipitate dissolved on warming. The determination of zirconium by direct weighing was not possible since the complex was contaminated with the reagent.

Separation of foreign ions :

Solution containing known amounts of different foreign ions with zirconium were mixed with a 5% (w/v) tartaric acid solution. The amount of tartaric acid was 10-15 times the total ions. Addition of reagent (20 times the amount of zirconium) and the adjustment of pH were made according to the general procedure. The ions Ca^{+2}(100 mg), Mg^{+2} (100 mg), Ba^{+2}(100 mg), Sr^{+2}(100 mg), Be^{+2}(50 mg), Al^{+3}(100 mg), Ni^{+2}(80 mg), Co^{+2}(100 mg), Cu^{+2} (100 mg), Zn^{+2}(100 mg), Cd^{+2}(100 mg), As^{+3}(100 mg), Sn^{+2}(80 mg), Hg^{+2}(80 mg), UO_2^{+2}(60 mg), Th^{+4}(60 mg), Mn^{+2}(100 mg), Cr^{+3}(100 mg), Bi^{+3} (100 mg), Ce^{+3}(60 mg), Br^-(50 mg), I^-(50 mg) and BO_3^{-3}(50 mg) did not interfere. Only Ti(IV), V(V), Ce(IV), Fe(III), Mo(IV), WO_4^{-2}, Nb^{+5}, Ta^{+5} and Hf(IV) interfered. To remove their interfering effect iron was masked by thioglycollic acid ;

titanium, vanadium and cerium by hydrogen peroxide. Molybdenum, tungsten, niobium and tantalum were removed by keeping the acid concentration high and by hot filtration when zirconium alone remained in solution. After filtration, zirconium was precipitated in the usual way at the required *p*H. The interference of hafnium could not however be removed.

Standard Deviation :

The standard deviation for sixteen determinations of zirconium (containing 8.8 mg of the metal oxide) with N-phenyl-o-tolyl hydroxylamine was ±0.012.

Metal ion Added	ZrO_2 Taken (mg)	ZrO_2 Found (mg)	Relative mean error (%)	Metal ion Added	ZrO_2 Taken (mg)	ZrO_2 Found (mg)	Relative mean error (%)
Fe(II)				WO_4^{-2}			
80 mg	8.80	8.80	+0.057	60 mg	8.80	8.80	±0
80 mg	8.80	8.81		60 mg	8.80	8 80	
Ti(IV)				Nb^{+5}			
100 mg	8.80	8.79	−0.171	50 mg	8.80	8 81	+0.171
100 mg	8.80	8.78		50 mg	8.80	8.82	
Ce(IV)				Ta^{+5}			
50 mg	8.80	8.80	+0.057	10 mg	8.80	8.78	−0.057
50 mg	8.80	8.81		10 mg	8.80	8.81	
MoO_4^{-2}				VO_3^-			
100 mg	8.80	8.78	−0.171	60 mg	8.80	8.81	+0.057
100 mg	8.80	8.79		60 mg	8.80	8.80	

References

1. A. K. Majumdar and B. K. Pal, *J. Indian Chem Soc.*, 1965, **42**, 43.
2. A. K. Majumdar and G. Das, *Anal. Chim. Acta*, 1964, **31**, 147.
3. A. K. Majumdar and M. K. Das, *Anal. Chim. Acta*, 1970, **50**, 243.
4. B. K. Pal, Ph.D. Thesis, Jadavpur University, 1964.
5. J. Welcher Frank, Organic Analytical Reagents, Vol. III, 1st published 1947, p. 379.
6. D. E. Ryan, *Canad. J. Chem.*, 1960, **38**, 2488.
7. I. P. Alimarin and S. Tung, Chaing Tse, *Talanta*, 1962, **9**, 9.

Studies on EGTA Complexes of VO_2^+ by Spectrophotometry

Arabinda K. Das* and Amiya Kumar Chakraburtty

Department of Chemistry, Jadavpur University, Calcutta-700 032

Manuscript received 13 February 1979, revised 17 March 1980, accepted 19 May 1980

EDTA (H_4Y) forms a complex compound VO_2Y^{-3} with pentavalent vanadium with stability constant, log K = 18.05 in 0.1*M* $NaClO_4$ medium. At *p*H values below about 3.5 the species VO_2HY^{-2} is formed and the acidic dissociation constant of this compound is $pK_a = 3.60$[1]. The equilibrium constant for the reaction $VO_2^+ + Y^{-4} = VO_2Y^{-3}$ in 0.1*M* KCl medium was also determined by other authors to be log K = 15.55. Nothing is known about the complex formed by pentavalent vanadium with ethylene glycol *bis*(aminoethyl ether)-N,N,N',N'-tetraacetic acid (EGTA or H_4L), a complexing agent analogous to EDTA.

Experimental

EGTA was obtained from Pfaltz and Bauer, Inc. and it was purified by crystallisation from hot water. Ammonium vanadate was E. Merck AG grade. All spectrophotometric studies were made by using an EC spectrophotometer model GS 865A and all *p*H measurements were made by using an EC expanded scale *p*H meter model *p*H 821A.

To a known volume of an ammonium vanadate solution was added a known solution of disodium salt of EGTA. The *p*H of this mixture was adjusted with dilute $HClO_4$ or NaOH solution. The whole mixture was then brought to a known volume in a measuring flask while the ionic strength was kept at approximately 0.1*M* by addition of $NaClO_4$ solution. The temperature was Ca. 22°. The *p*H of each of these solutions was measured in the *p*H meter with an agaragar-KCl salt bridge. Next, the absorbance of the same solution was measured in the spectrophotometer. All the measurements were carried out at 22°.

After a study was made with *p*H versus molar absorbance of the solution at 340 nm in the whole *p*H range (2 to 13), the data was plotted in Fig. 1. Next, in the *p*H range where the formation of the

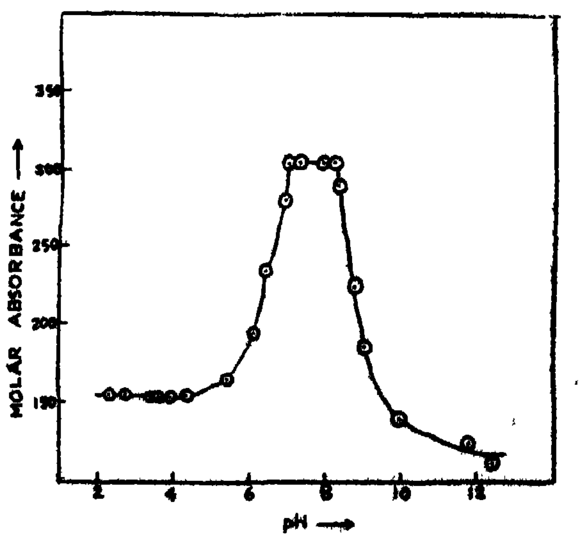


Fig. 1. Molar absorbance of vanadium at 340 nm in an excess of EGTA as a function of pH + $C_V = 2 \times 10^{-4} M$, $C_{EGTA} = 1 \times 10^{-3} M$.

* Present address : Department of Chemistry, The University of Burdwan, Burdwan-713 104.

concerned species occur the absorbances at different pH's were measured at different wavelengths. The experimental data are shown in Tables 1 and 2.

TABLE 1—DETERMINATION OF THE ACIDIC DISSOCIATION CONSTANT

C_V(M)	C_{EGTA}(M)	pH	A_b^{540}	A_a^{540}	A_m^{540}	pK_a
2×10^{-3}	1×10^{-3}	5.4	0.61	0.31	0.33	5.546
2×10^{-3}	1×10^{-3}	6.1	0.61	0.31	0.39	5.589
2×10^{-3}	1×10^{-3}	6.6	0.61	0.31	0.49	5.424
2×10^{-3}	1×10^{-3}	6.9	0.61	0.31	0.56	5.201
			A_b^{540}	A_a^{540}	A_m^{540}	
1×10^{-3}	1×10^{-3}	5.6	0.42	0.28	0.34	5.462
1×10^{-3}	1×10^{-3}	6.0	0.42	0.28	0.38	5.426
1×10^{-3}	1×10^{-3}	6.4	0.42	0.28	0.40	5.471
1×10^{-3}	1×10^{-3}	6.8	0.42	0.28	0.41	5.545
			A_b^{580}	A_a^{580}	A_m^{580}	
1×10^{-4}	1×10^{-3}	5.5	0.19	0.09	0.14	5.500
1×10^{-4}	1×10^{-3}	5.9	0.19	0.09	0.15	5.532
1×10^{-4}	1×10^{-3}	6.3	0.19	0.09	0.17	5.698
1×10^{-4}	1×10^{-3}	6.5	0.19	0.09	0.18	5.546

known equation :

$$\frac{C_b}{C_a}=\frac{A_m-A_a}{A_b-A_m} \quad \ldots (3)$$

where $C_a=[VO_2HL^{-2}]$, $C_b=[VO_2L^{-3}]$

A_b = measured absorbance in the pH range 7.0-8.2,

A_a = measured absorbance in the pH range 2.7-4.5, and

A_m = measured absorbance at the inter- mediate pH between 4.5 to 7.0.

The expression for the dissociation constant of the species VO_2HL^{-2} is given by

$$k_a=\frac{[H^+].C_b}{C_a} \quad \ldots (4)$$

TABLE 2—DETERMINATION OF THE FORMATION CONSTANT

$C_V=C_{EGTA}$(M)	pH	log β_{HL}	$A^{580}_{VO_2HL}$	$A^{580}_{VO_2}$	A^{580}	α	log K_{VO_2HL}
1×10^{-3}	3.5	−4.93	0.54	0.23	0.35	0.613	7.946
1×10^{-3}	4.0	−4.41	0.54	0.23	0.39	0.484	7.754
1×10^{-3}	4.5	−3.90	0.54	0.23	0.45	0.290	7.830
1×10^{-3}	5.0	−3.40	0.54	0.23	0.49	0.193	7.737
			$A^{580}_{VO_2HL}$	$A^{580}_{VO_2}$	A^{580}		
5×10^{-3}	3.8	−4.57	0.33	0.15	0.23	0.555	7.730
5×10^{-3}	4.3	−4.11	0.33	0.15	0.27	0.333	7.186
5×10^{-3}	4.8	−3.60	0.33	0.15	0.29	0.111	7.761
5×10^{-3}	5.3	−3.10	0.33	0.15	0.32	0.055	7.896

Results and Discussion

Fig. 1 shows that ammonium vanadate solution when titrated with disodium salt of EGTA, the acidity constant remains the same in the pH range 7.0-8.2 until the equivalent point :

$$VO_3^- + H_2L^{-2} = VO_2L^{-3} + H_2O \quad \ldots (1)$$

In solutions at pH values below 7.0, another complex is formed,

$$VO_2L^{-3} + H^+ = VO_2HL^{-2} \quad \ldots (2)$$

The analogous EDTA complexes, e.g., VO_2Y^{-3} and VO_2HY^{-2} have been established earlier[1,3]. For strongly acidic solutions (e.g., at pH below 9.3), the acid ligand EGTA starts separating out. In the most basic solutions (e.g., at pH values higher than 8.2) vanadates are formed[2].

At a particular wavelength, it is possible to calculate the concentrations of different species by well

Combining equations (3) and (4)

$$k_a=\frac{[H^+].(A_m-A_a)}{(A_b-A_m)} \quad \ldots (5)$$

The expression for the formation constant of the species VO_2HL^{-2} is given by a similar equation described previously[1].

$$K_{VO_2HL}=\frac{(1-\alpha)}{2_{\beta_{HL}}C} \quad \ldots (6)$$

where

$$\alpha=\frac{A_{VO_2HL}-A}{A_{VO_2HL}-A_{VO_2}} \quad \ldots (7)$$

β_{HL} = fraction of EGTA not bound to VO_2^+ appears as HL^{-3} and

$$\beta_{HL}=\frac{[H^+].\beta_L}{k_4} \quad \ldots (8)$$

with $$\beta_L = \left[\frac{[H^+]^4}{k_1k_2k_3k_4} + \frac{[H^+]^3}{k_2k_3k_4} + \frac{[H^+]^2}{k_3k_4} + \frac{[H^+]}{k_4} + 1\right]^{-1} \quad \ldots (9)$$

The values of acid dissociation constants k_1, k_2, etc., were obtained from a handbook[4].

However, the expression for the formation constant will be

$$K_{VO_2L} = \frac{K_{VO_2HL} \cdot k_{VO_2HL}}{k_4} \quad \ldots (10)$$

The obtained values are compared with corresponding values of EDTA complexes[1,2]. It transpires that the species $VO_2H(EDTA)^{-2}$ ($pK_a = 3.60$) is more acidic than $VO_2H(EGTA)^{-2}$ ($pK_a = 5.49$) whereas the stability values of the species VO_2H-$(EDTA)^{-2}$ (11.39) and VO_2 $(EDTA)^{-3}$ (18.05) are more than the corresponding $VO_2H(EGTA)^{-2}$ (7.73) and $VO_2(EGTA)^{-3}$ (11.18). This may be attributed to the steric effect due to longer linking chain between the two nitrogen atoms separating the carboxylic acid groups apart in the EGTA molecule as compared to the shorter separation in EDTA. The plateau region of the VO_2^+-EGTA system (Fig. 1) is shorter than that of VO_2^+-EDTA system[1] which may be due to the same reason.

References

1. A. Ringbom, S. Siitonen and B. Skrifvars, *Acta Chem. Scand.*, 1957, **11**, 551.
2. L. Przyborowski, G. Schwarzenbach and Th. Zimmerman, *Helv. Chim. Acta*, 1965, **48**, 1556.
3. F. J. C. Rossotti and H. Rossotti, *Acta Chem. Scand.* 1956, **10**, 957.
4. Stability Constants, (Supplement No. 1), Special Publication 25, Chemical Society, London, 1971.

Estimation of Thiourea, Allyl Thiourea and Tolyl Thiourea by Sodium N-Chloro-*p*-Toluene Sulphonamide†

K. V. Uma and S. M. Mayanna*

Department of Chemistry, Central College, Bangalore-1

Manuscript received 7 February 1979, revised 29 May 1979, accepted 19 May 1980

The mechanism of oxidation of thioureas has been the subject of many investigations[1]. Thiourea and its derivatives are generally oxidised to the corresponding disulphide[2], although instances of oxidation beyond the disulphide stage are also known[3]. Several oxidising agents have been used for assaying these compounds[4-9] and an excellent review of the subject by Balwanth Singh *et al.*[10] is noteworthy. Thioureas find a number of industrial applications in rubber valcanization, electrodeposition of metals, corrosion inhibition, photography and in polymer, textile and agricultural industries. Sodium N-chloro-*p*-toluene sulphonamide (Chloramine-T), has been used in estimations of thiourea and its derivatives in slightly concentrated sulphuric acid and at high temperatures[11]. However, this method is less accurate because of the decomposition of chloramine-T at high temperatures[12]. The present communication deals with the estimation of thiourea (TU), allyl thiourea(ATU) and tolyl thiourea(TTU) by chloramine-T under mild experimental conditions.

Chloramine-T (E. Merck) was purified[13] and used. All other reagents were of analytical grade. Solutions were prepared using triple distilled water. Chloramine-T(CAT) solution was standardised by iodometric method.

Since the oxidation reactions are not instantaneous under the given experimental conditions and the optimum medium contains sufficient amount of HCl, direct visual titration and potentiometric titration were not carried out. Hence, back titration procedure was adopted for the estimations of these compounds.

In preliminary experiments with CAT, known amounts of TU, ATU and TTU prepared in the appropriate buffer[14] or solvent were added to a known and excessive volume (10-20%) of CAT solution in iodine flasks at 30°. The reaction mixtures were set aside for various intervals of time, with occasional shaking. Then the excess of CAT was determined by back titration. A typical set of results for the extent of oxidation of TU, ATU and TTU in different media are given in Table 1. Oxidations of TU and ATU are not reproducible and non-stoichiometric in various media other than HCl solutions. The % oxidation increases gradually as the concentration of HCl increases, but the increase becomes rapid at or above 0.5*N* HCl. However,

Table 1—Extent of Oxidation of Thiourea, Allyl Thiourea and Tolyl Thiourea in Different Media with Excess of Chloramine-T at 30°C

Medium	%Oxidation			Medium	%Oxidation		
	TU	ATU	TTU		TU	ATU	TTU
0.6*M* HCl	100.1	100.2	48.0	*p*H*2	77.4	91.1	94.4
0.5*M* HCl	99.2	100.1	49.6	*p*H†3	80.8	93.0	85.8
0.4*M* HCl	97.7	100 0	49.6	*p*H**4	84.5	93.6	70.5
0.3*M* HCl	96.5	97.0	50.4	*p*H**5	92.1	94.0	68.7
0.2*M* HCl	93.6	92.1	51.1	*p*H**6	95.0	96.0	65.6
*p*H*1	92.9	89.5	70.4	*p*H††7	96.5	98.0	63.0

[CAT] taken $5\times10^{-3}M$, [TU], [ATU] and [TTU] taken $7\times10^{-4}M$
*HCl-KCl buffer, **Sodium acetate-acetic acid buffer,
†Potassiumbiphthalate-HCl buffer. ††Borax-boric acid buffer.
Time : 30 minutes for ATU and TTU, 45 minutes for TU.

† Presented in the Annual Convention of Chemists, 1978.

the oxidation reaction of TTU is stoichiometric and rapid in $8M$ CH_3COOH solution containing $0.5M$ HCl.

Recommended Procedure :

Prepare aqueous solutions of TU, ATU ($0.01M$). Add aliquots containing 0.1-2.5 mM to measured excessive (10-20%) volume of $0.01N$ CAT containing enough HCl to make the overall acid concentration (0.5-$0.6M$). In the case of TTU, add sufficient amounts of CH_3COOH and HCl to the medium to get the resulting concentrations $8M$ and $0.5M$, respectively. Shake the mixtures and keep it in a thermostat at 30° for 30 min in the cases of TTU and ATU and 45 min for TU. Add 10 ml of 10% KI solution along with 10 ml of $2N$ H_2SO_4. Titrate the liberated iodine with standard thiosulphate solution. Run a blank experiment with CAT under identical conditions without TU, ATU and TTU. Amounts (mgs) of TU, ATU and TTU in the sample solutions are given by the equation

$$X = Wy\,(V_1 - V_2)$$

where y is the normality of the thiosulphate solution, V_1 is the blank titre value and V_2 is the test titre value. W takes the values of 9.5, 9.71 and 13.88 for TU, ATU and TTU respectively. From the reaction products, sulphate and *p*-toluene sulfanamide are isolated and characterised. In the cases of ATU and TTU substituted amines are detected.

Some typical results of analysis of TU, ATU and TTU in aqueous solutions are given in Table 2. The

TABLE 2—ESTIMATION OF THIOUREA, ALLYL THIOUREA AND TOLYL THIOUREA BY CHLORAMINE-T AT 30°C

Thiourea*		Allyl Thiourea**		Tolyl Thiourea***	
taken (mg)	found (mg)	taken (mg)	found (mg)	taken (mg)	found (mg)
1.90	1.91	2.32	2.30	1.66	1.67
3.80	3.77	4.64	4.60	3.32	3.32
7.60	7.65	5.81	5.85	4.98	4.94
11.40	11.38	11.62	11.62	6.64	6.67
15.20	15.25	17.20	17.05	8.30	8.40
19.00	19.10	23.20	23.40	12.45	12.40
22.80	22.70	29.25	29.40	16.61	16.45
30.40	30.35	34.86	34.65	20.77	20.77
38.00	38.30	40.66	40.39	24.98	24.98
45.60	45.40	46.40	46.80	29.05	29.15
53.20	53.35	50.20	49.60	33.20	33.45
60.80	60.50	56.00	54.50	37.35	37.10

*$0.6M$ HCl **$0.5M$ HCl ***$8M$ $CH_3COOH + 0.5M$ HCl
Time : 30 minutes for ATU and TTU, 45 minutes for TU.

values obtained are accurate within 1%. The detailed study of oxidation of TU, ATU and TTU by CAT has brought out the following facts :

(1) ATU and TTU undergo oxidation with 12 electron change, whereas TU is oxidised with 8 electron change.

(2) Foreign ions such as nitrate, perchlorate and sulphate ions have no influence (up to ionic strength 0.25)

(3) Chloride ion has slight effect on the rate of oxidation.

(4) The stoichiometry is unaffected by the reversal of the order of addition of oxidant and thioureas.

In acidic chloride solutions CAT gives several oxidising species[13,16] such as $RNCl_2$, RNHCl, H_2OCl^+ and Cl_2, which may oxidise these organic substrates. Kinetics of oxidation of TU, ATU and TTU is under detailed investigation which may throw light on the mechanism of oxidation by CAT.

References

1. P. RAIZMAN and Q. E. THOMSON in "The Analytical Chemistry of Sulphur and its Compounds", Part II, T.H. KARCHIMER, Ed. Chemical Analysis vol. 29. Wiley-Interscience, New York, 1972, p. 668.
2. B. SINGH and B. C. VERMA, *Z. Anal. Chem.*, 1963, **196**, 439.
3. T. V. KRAMAREVA, V. M. SHULMAN and C. G. LAVREUOVA, *Isv Sibirak otd Akd Nauk SSSR, Ser. Khim. Nauk.*, 1964, **2**, 101.
4. B. SINGH, B. C. VERMA and M. S. SARAN, *J. Indian Chem. Soc.*, 1962, **39**, 211.
5. R. CUTHILL and C. ATKINS, *J. Soc. Chem. Ind.*, 1937, **56**, 5T.
6. B. SINGH, B. C. VERMA and M. S. SARAN, *J. Indian Chem. Soc.*, 1962, **39**, 490.
7. B. SINGH, B. C. VERMA and M. S. SARAN, *Proc. Natl. Acad. Sci., Indian Sec.*, 1963, **A33**, 305.
8. B. SINGH and B. C. VERMA, *J. Indian Chem. Soc.*, 1963, **40**, 39.
9. B. SINGH, B. C. VERMA and Y. K. KALIA, *Indian J. Chem.*, 1964, **2**, 124.
10. B. SINGH and B. C. VERMA, *J. Sci. Ind. Res.*, 1965, **24**, 536.
11. B. SINGH, B. C. VERMA and T. K. KALIA, *J. Indian Chem. Soc.*, 1963, **40**, 697.
12. A. GEORGE, M. Sc. dessertation, Bangalore University, 1978.
13. J. C. MORRIS, J. A. SALAZON and M. A. WINEMAN, *J. Amer. Chem. Soc.*, 1948, **70**, 2036.
14. "Findlay's Practical Physical Chemistry" revised by B. P. LEVITT, 9th Eds. Longmann, 1973, p. 303 and 311.
15. K. V. UMA and S. M. MAYANNA, *Bull. Chem. Soc., Japan*, 1978, **51**, 1047.
16. E. D. HUGHES and C. K. INGOLD, *Quart. Rev.*, (London), 1952, **6**, 34.

Iodometric Determination of Certain Organic Acids

S. M. NEMA, O. P. SONI and R. M. VERMA*

Department of Post-Graduate Studies and Research in Chemistry, University of Jabalpur, Jabalpur

Manuscript received 4 June 1977, revised 4 April 1978, accepted 19 May, 1980

AN iodometric determination of carboxyl group in certain organic acids at room temperature has been described.

The well-known analytical reaction between iodide and iodate in presence of acid solution

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

has been used for the determination of acids ; this is used as an alternative, often more accurate to the usual titration with alkali[1]. Iodide present is oxidized, in amounts equivalent to the acid present, to iodine which is titrated with thiosulphate. The position of the equilibrium of the reaction is strongly influenced by the pH of the solution. The iodometric method gives excellent result even with dilute solutions of strong acids provided the iodide-iodate mixture is allowed to stand for at least 15 minutes before titration[2]. This method. however, fails in case of weak acids when the pH at the end-point is too high to effect complete reaction[2,3]. Bruhns[4] achieved quantitative reaction in about half an hour by adding calcium or magnesium chloride to the reaction mixture. But this procedure is applicable only to organic hydroxy acids. Another modification due to Kolthoff[5] involves the addition of a measured excess of thiosulphate to acid solution containing iodide and iodate and subsequent titration of the residual thiosulphate with iodine. With dilute solutions the reaction is much slower making the reaction unsuitable for use in the quantitative analysis of weak acids. This modification has been adopted for estimating the acid content in various products ; the time allowed for the reaction being 2-24 hours[7-9]. These procedures require much time moreover, there is a possibility of thiosulphate reacting with acid. The reaction time cannot be shortened by heating due to volatility of iodine. In order to speed up the iodometric determination of weak acids, the reaction between certain organic acids, iodide and iodate was studied from analytical view point and the following inferences were drawn.

(a) In a set of experiments, the volume of iodide and iodate solution was increased stepwise. But even a large excess of iodate and iodide solution could not make the reaction quantitative in 15-30 minutes at room temperature. The slow reaction rate is due to increase in the overall volume of the reaction mixture as iodide and iodate solutions are added. This view was supported by a study on the dilution effect which revealed that there is a sharp fall in the reaction velocity with increase in the volume of the reaction mixture. It follows that the reaction rate can be accelerated by keeping the volume of the reaction mixture at a minimum.

(b) In view of the above observation, the addition of suitable amounts of iodide and iodate in the solid form was attempted which made the reaction to go to completion in 2-10 minutes at room temperature. The reaction time could be extended up to 30-60 minutes with no adverse effects. Likewise, the addition of even undue large excess of solid iodide and iodate did not interfere with the results.

On the basis of the afore-mentioned observations, a procedure has been evolved for the iodometric determination of sixteen aliphatic acids.

Experimental

The following solutions were prepared using Chemicals of A. R. grade.

0.1N solutions of different acids were prepared by standardization with alkali. 0.05. 0.025, 0.01 and 0.005N solutions were then prepared by suitably diluting 0.1N solution.

0.1N thiosulphate was prepared and standardized with standard iodate. 0.05, 0.025, 0.01 and 0.005N solutions were prepared by diluting with conductivity water.

Recommended Procedure :

5-20 ml of the acid sample containing 0.05-0.5 meq. of carboxyl group is pipetted into a 100 ml iodine flask. 1-5 g of solid potassium iodide and 1-3 g of solid potassium iodate are added and the contents of the flask are stirred using a magnetic stirrer. After waiting for 2-10 minutes the liberated iodine is titrated with thiosulphate solution (0.05-0.005N) through a microburette using starch as indicator.

1 ml of 0.01N thiosulphate = 0.45 mg of carboxyl group.

Results and Discussion

In titrating a dilute solution of a weak acid with 0.01N sodium hydroxide solution, the recognition of the end-point is not easy because the phenolphthalein colour fades rapidly[10]. This difficulty increases with increasing dilution of the titrant solution. In the proposed iodometric method there is not much difficulty in detecting the end-point when 0.005N or even more dilute solution of thiosulphate

* To whom correspondence should be addressed.

is used as the titrant. Furthermore, while determining the acid content of a product containing a component capable of reacting with alkali, the titration with alkali cannot yield correct results. For example, in estimating carboxy acids in lac, the resin present undergoes saponification[6]. In certain products which are slightly coloured the neutralization indicators may not be very suitable. For these reasons attempts were made[4,5] to evolve an iodometric method for the estimation of weak acids—but these attempts had limited applicability and were time consuming. Kolthoff's modified procedure[5] has been adopted by several workers[7-9] for estimating the acid content in a number of products, but the time required for the completion of the reaction is 2-24 hours. The proposed procedure is simple, rapid and accurate ; being iodometric it possesses sharp end-point, the amounts of reagent and reaction time are not critical and hence it can be adopted with advantage for the titrimetric determination of dilute solutions of weak acids.

TABLE 1—IODOMETRIC DETERMINATION OF CERTAIN ORGANIC ACIDS

(Room Temperature 30-35°)

Sl. No.	Acids	KIO_3 added (g)	KI added (g)	Reaction time (mins)	%Deviation* Proposed method	Comparison method**
1.	Formic	1	2	2	0.1	0.5
2.	Acetic	2	2	5	0.2	0.6
3.	Monochloroacetic	0.5	0.5	2	0.2	0.6
4.	Dichloroacetic	0.5	0.5	2	0.1	0.5
5.	Trichloroacetic	0.5	0.5	2	0.2	0.7
6.	Propionic	2	5	5	0.4	0.9
7.	β-chloropropionic	1	2	2	0.3	0.8
8.	Butyric	2	5	5	0.5	0.9
9.	Oxalic	1	1	2	0.2	0.6
10.	Malonic	2	5	10	0.3	0.7
11.	Succinic	2	5	10	0.5	0.9
12.	Glycollic	1	2	5	0.2	0.8
13.	Malic	1	1	2	0.2	0.7
14.	Tartaric	1	1	2	0.4	0.6
15.	Citric	1	1	5	0.3	0.7
16.	Crotonic	1	2	5	0.2	0.6

* Average of six determinations.

** In these titrations phenolphthalein colour faded rapidly. The first appearance of red colour was taken as the end-point.

In case of acids 3, 4 and 5 iodide and iodate solutions can also be employed. In case of acid 10, the reaction-time should not exceed 15 mins otherwise low results are obtained.

Table 1 shows the amount of potassium iodide and potassium iodate to be added and reaction time to be allowed in case of sixteen acids examined. A comparative study of determination of these acids at micro level (0.05 meq. of acid present in 10 ml of assay solution) by iodometry and alkalimetry has also been presented in this table. The concentration of the titrant solution (sodium thiosulphate or sodium hydroxide) used was 0.005*N*.

Acknowledgement

Thanks are due to Professor G. S. Misra, Dean, Faculty of Science, University of Jabalpur, Jabalpur for providing facilities for this work. One of the authors (S.N.N.) acknowledges financial assistance from the University of Jabalpur, Jabalpur.

References

1. M.R.F. ASWORTH, "Titrimetric Organic Analysis , Part II, Interscience, London, 1965, p. 477.
2. I. M. KOLTHOFF, *Pharm. Weekblad*, 1920, **57**, 63.
3. M. GROGER, *Z. angew. Chem.*, 1890, **3**, 353.
4. G. BRUHNS, *Z. anal. Chem.*, 1916, **55**, 45.
5. I. M. KOLTHOFF, *Chem. Weekblad*, 1926, **23**, 260.
6. N. R. KAMATH and V. B. MAINKER, *Anal. Chem.* 1950, **22**, 724.
7. P. VIELES, *Bull. Soc. Chim.*, 1939, **6**, 1127.
8. H. G. DASSLER, *Pharm. Zentralhalle*, 1962, **101**, 409.
9. H. VAILLANT, *Mikro Chim. Acta*, 1963, 98.
10. T. B. SMITH, "Analytical Processes", 2nd Ed., *Arnold*, London, 1952, p. 226.

Polarographic Study of Ni(II)-Succinimide System

(KM.) KRISHNA,* (KM.) ANJU VARSHNEY

and

M. C. DUBEY

Department of Chemistry, Agra College, Agra, India

and

S. K. JHA

Institute de Quimica, Universidade Federal da Bahia, Salvador, Bahia, Brazil

Manuscript received 2 January 1979, revised 18 September 1979, accepted 9 April 1980

A survey of the literature reveals that although the behaviour of Ni(II) in presence of various complexing media has been investigated but very few studies have been reported with amides[1,2]. Ni(II)-succinimide system has not been investigated so far. It was, therefore, thought worthwhile to study the polarographic behaviour of Ni(II) in the presence of succinimide.

Experimental

$Ni(NO_3)_2.6H_2O$ was used as the source for depolarizer metal ion, Ni(II). Supporting electrolyte was KCl. The potassium salt of succinimide was prepared from succinimide and KOH. All the chemicals used were of high purity (B.D.H or S. Merck) and all the solutions were prepared in doubly distilled water. In the final polarographic

* To whom all correspondence should be directed.

solution the Ni(II) concentration was kept as 1 mM. The concentration of succinimide was varied by adding different amounts of the stock solution of potassium-succinimide. The pH of the final solution was maintained by adding a dilute solution of NaOH. A manual polarograph in conjunction with a polyflex galvanometer was used to record polarograms. Deoxygenation of the solution was done by passing nitrogen gas. The dropping mercury electrode consisted of a standard capillary (E. H. Sargent & Co., USA) and had following characteristics : $m^{2/3} t^{1/6} = 2.8446$ $mg^{2/3}$ $sec^{-1/2}$, $t = 3.48$ sec. in $0.5M$ KCl at -1.3 V vs S.C.E,, $h_{corr} = 63.3$ cm. Slope and $E_{1/2}$ values have been calculated by least square method from $E_{d.e.}$ vs log $i/i_d - i$ plots.

Results and Discussion

The linearity of the plots of i_d vs $\sqrt{h}$ reveals the diffusion controlled nature of the system. The irreversible nature of the electrode reaction is established by the slope values and also from log i vs log h plots[3]. For a totally irreversible process the current at the foot of the wave should be independent of the height of the mercury column while the limiting current should be proportional to $\sqrt{h}$. Between the two extremes both diffusion and kinetics of the electrode reaction affect the current. At various stages of a polarogram, starting from the "foot" to "levelling off" positions log i-log h plots were straight lines with slope varying from 0 to 0.5.

It was observed that the variation of the concentration of the ligand affected the pH of the resultant solution. Therefore, to ensure that the shift in $E_{1/2}$ was solely due to the complexation and not due to pH change resulting from different concentrations of ligand, it was found necessary to maintain pH.

A solution of 1 mM Ni(II) without any potassium succinimide had pH 5.9. Addition of $0.04M$ potassium succinimide altered the pH to 6.8. Attempt to increase pH beyond pH 8 resulted in turbidity. No shift in $E_{1/2}$ was observed at pH 6. This allowed only a very small range of pH. Maximum shift which signifies maximum stability of complex was observed at pH 8.

TABLE 1

Conc. of Ni(II)	Conc. of ligand M	pH	$-E_{1/2}$ V vs S.C.E.	$\Delta E_{1/2}$
1 mM	0.00	7.0	1.010	0.150
	0.04		0.860	
1 mM	0.00	8.0	1.010	0.180
	0.04		0.830	

Kinetics of the electrode process as a function of ligand concentration was studied at pH 8. αn_a values showed an increase up to the ligand concentration of 0.6 mM and then decreased. An attempt to est n_a apparently leads to a conclusion that because for totally irreversible systems, as present one is, α should be less than 0.5. How according to Meites[4] only a single electron ca transferred at a time and a value of n_a exceedi should merely mean that the successive step too nearly simultaneous to be distinguished or time scale implicit in the polarographic meas ment. Thus whether n_a is 1 or 2 the change in values which at no stage vary by a factor between successive values can only be due to ch in α. Increase in α values signifies shift tow reversibility. Thus it may be concluded that Ni(II)-succinimide complex is reduced more e than the aqueous Ni(II) ion[5] which is in confor with other ligands in case of Ni(II).

Decrease in αn_a values between 0.08-0.1M po ium-succinimide concentration could not explained for the moment, however, it was in formity with negative shift in $E_{1/2}$ with increa ligand concentration beyond certain limits observed by other workers[6] in case of other liga

TABLE 2

$\mu = 0.5$, $pH = 8.0$, Temp. $= 25 \pm 0.1$°C

[Succinimide] M	$-E_{1/2}$ V vs S.C.E.	Slope	αn_a
0 00	1.045	0.115	0.5141
0 01	0.910	0.100	0.5915
0.02	0.900	0.100	0.5915
0 04	0.895	0.095	0.6220
0.06	0.900	0.095	0.6290
0.08	0.910	0.100	0.5915
1.00	0.910	0.100	0.5915

Acknowledgement

Authors are thankful to the Principal, College, Agra for providing necessary facilities Dr. Mukhtar Singh for his interest in the work.

References

1. E. T. TUICHIEV, L. E. KORNEVA and A. M. MURTAZ Mater Tubileinoi. Resp. Nauchn. Konf. Pasvyashch. 50-Letyiyu Obraz USSR, Sept., 1972 (1972) 139-61 ; *C. A.*, 1975, **82**, 161780n.

2. R. TAMAMUSHI and N. TANAKA, *Bull. Chem. Soc. J* 1946, **22**, 227.

3. P. DELAHAY, *J. Amer. Chem. Soc.*, 1951, **73**, 4944 ; JHA, S. JHA, J. C. KHATRI and M. SINGH, *I J. Chem.*, 1977, **15A**, 184.

4. L. MEITES, "Polarographic Techniques, Intersc Publishers, 1967, 246.

5. D. R. CROW, "Polarography of Metal Complexes", Aca Press, New York, 1969, p. 57.

6. D. R. CROW, "Polarography of Metal Complexes", Aca Press, New York, 1969, p. 56.

Standard Enthalpy of Formation of Bismuthyl Nitrate

LAMBODAR THAKUR,* A. K. THAKUR, R. PRASAD

and

M. F. AHMAD

Post-Graduate Department of Chemistry, Bhagalpur University, Bhagalpur-812 007, India

Manuscript received 17 August 1979, revised 3 March 1980, accepted 9 April 1980

AT room temperature, bismuth dissolves in fairly concentrated nitric acid solutions (>6*M*-HNO_3) liberating NO gas. The acid solution on evaporation produces a white residue which on dyring yields anhydrous crystals of bismuthyl nitrate, $BiONO_3$(c). The standard enthalpy of formation of $BiONO_3$(c) has not been reported even in recent compilations[1-3].

We report in this work the enthalpies of solution of bismuth metal, bismuthyl nitrate, nitric acid and water in their standard states in 11*M*-HNO_3 solution. From the enthalpies of solution, ΔH_{soln}, the standard enthalpy of formation of bismuthyl nitrate can be calculated by eqns. (1) and (2).

$$\Delta H_f^\circ BiONO_3(c) = 2\Delta H_f^\circ HNO_3(l) - \Delta H_f^\circ H_2O(l) - \Delta H_f^\circ NO(g) + \Delta H \quad \ldots (1)$$

where

$$\Delta H = \Delta H_{soln} Bi(c) - \Delta H_{soln} BiONO_3(c) + 2\Delta H_{soln} HNO_3(l) - \Delta H_{soln} H_2O(l) \quad \ldots (2)$$

Experimental

Pure bismuth metal (99.999%) was obtained from Nuclear Fuel Complex, Hyderabad(India). It was finely cut and sealed in fragile bulbs under dry nitrogen gas[4]. Bismuthyl nitrate was obtained by dissolving the pure metal in 11*M*-HNO_3 and the resulting solution evaporated to dryness and finally baked at 115° for several hours. The compound was analysed for bismuth and nitrogen (Found : Bi, 71.2 ; N, 4.9 ; Calc. for $BiONO_3$(c) : Bi, 72.8 ; N, 4.9%). The white crystalline compound was sealed in fragile bulbs as above. On strongly heating a weighed sample of $BiONO_3$(c), the loss in weight corresponded with the formation of a yellowish-white residue of Bi_2O_3 from $BiONO_3$(c). BDH 'AnalaR' nitric acid (≈95%) was used without further concentration.

A closed-system calorimeter described earlier[5] was used. Briefly, it consists of a 200 ml 'pyrex' silvered Dewar vessel with an attachment of a water-tight perspex lid. A number of accessories like a temperature sensor (10KΩ-thermistor), a calibration heater (manganin heater), a mercury-seal stirrer, a fragile ampoule holder, an ampoule breaker, and B_{14} coned inlet and outlet tubes were provided, all of which passed through the grooves cut across the transparent lid and held in fixed positions by vacuum O-rings sandwiched between the perspex sheets of the lid. The calorimeter was immersed completely in a thermostated water bath at 298 ± 0.1K. All measurements were made under an atmosphere of dry nitrogen.

* To whom correspondence should be addressed.

TABLE 1—ENTHALPIES OF SOLUTION OF SUBSTANCES IN 11*M*-HNO_3 AT 298 K

Substances	Weight (gms)	Concn. (mole/1)	H_{soln} kJ mole^{-1}	Mean
Bi(c)	0.0529	0.0014	−267.8	
	0.0560	0.0015	−286.6	−277.5±10.0
	0.0632	0.0017	−278.2	
$BiONO_3$(c)	0.2182	0.0043	−27.2	
	0.3077	0.0061	−29.2	−28.9±2.0
	0.3760	0.0074	−29.9	
HNO_3(l)	1.66299	0.1506	−11.2	
	1.68316	0.1527	−11.6	−11.4±0.3
H_2O(l)	0.99888	0.3171	−1.9	
	1.56625	0.4972	−1.8	−1.9±0.2
	1.92044	0.6097	−2.1	

Results and Discussion

Table 1 lists the enthalpies of solution of Bi(c), $BiONO_3$(c), HNO_3(l) and H_2O(l) in 11*M*-HNO_3 solution. No correction for the loss of heat of the calorimetric liquid due to the escape of evolved NO gas in the dissolution of bismuth metal has been made. However, it will have a minimal effect on the enthalpy of solution considering the limits of experimental uncertainty. Substituting the values of ΔH_{soln} from the table in eqn. (2) we get $\Delta H = -269.5$ kJ mole^{-1}. The standard enthalpies of formation of H_2O(l), HNO_3(l) and NO(g) are -285.8, −174.1 and +90.2 kJ mole^{-1} respectively[1]. On utilization of the above data in eqn. (1) we get $\Delta H_f^\circ BiONO_3(c) = -422.0 \pm 10$ kJ mol^{-1}. The average error has been estimated as twice the standard mean deviation.

Acknowledgement

The authors thank the U.G.C., New Delhi for a research grant.

References

1. D. D. WAGMAN, W. H. EVANS, I. HALOW, V. B. PARKER, S. M. BAILEY and R. H. SCHUMM, "Selected Values of Chemical Thermodynamic Properties", Technical Note 270-1, NBS, Washington, 1965.
2. R. C. WEAST, Ed., "Handbook of Chemistry and Physics", 59th edn., 1978-79, CRC Press, Florida.
3. N. A. LANGE, "Handbook of Chemistry", McGraw-Hill, New York, 1974.
4. L. THAKUR, M. F. AHMAD and R. PRASAD, *Indian J. Chem.*, 1978, **16A**, 661.
5. L. THAKUR, M. F. AHMAD and R. PRASAD, *Indian J. Chem.*, 1978, **16A**, 368.

A Reverse-Osmosis Membrane: Thermodynamic Evaluation of its Effective Thickness

SAROJ KUMAR SANYAL

Chemistry Department, Presidency College, Calcutta-700 073

Manuscript received 28 May 1979, revised 24 March 1980, accepted 9 April 1980

IN recent years, various studies, electron microscopy among them[1,2], have revealed that the cellulose acetate membranes, which have been successfully used in hyperfiltration (reverseosmosis) of saline water, are not homogeneous, and are characterised by very thin dense surface layers where the maximum salt-rejection takes place. Various hypotheses have been put forward to explain such rejection in terms of the failure of water to effectively hydrate the ions in this thin layer, and this is said to result from a change in structure of water (from bulk-water) inside the layer, due to its interaction with this dense layer, which behaves differently from the bulk-membrane phase. As a consequence, the salt is thrown out as a "precipitate". It is worth noting that the thermodynamic approach for diffusion also leads to the conclusion that the effective thickness of such membranes for water transport is indeed very small as compared to their total thickness, and this will be deduced in the present communication.

The membrane is considered, for the sake of simplicity, to be perfectly semi-permeable, i.e., only water can diffuse through it. The general form of Fick's first law for such transport process reads,

$$J_w = -D_w \frac{C_w}{RT} (\partial \mu_w/\partial x)_M \quad \text{.. (1)}$$

where J_w is the diffusion flux of water through the membrane (mol. cm^{-2}. sec^{-1}), D_w, the ordinary (isothermal) diffusion coefficient of water (cm^2. sec^{-1}), C_w, the "concentration of water" in the membrane (mol. cm^{-3}), $(\partial \mu_w/\partial x)_M$, the chemical potential gradient of water in the membrane (M), and this is the "driving force" for water-diffusion. Assuming that the salt-rejection is 100%, it is possible to write,

$$(\partial \mu_w/\partial x)_M = V_w(\partial_P/\partial x)_M \quad (2)$$

where V_w is the molar volume of water, and $(\partial_P/\partial x)_M$ is the pressure gradient applied across the membrane (in reality, it is the effective pressure gradient across the membrane).

It follows from equations (1) and (2),

$$J_w = -D_w \frac{C_w V_w}{RT}(\partial_P/\partial x)_M \quad \text{. (3)}$$

If now ρ_m is the density (g. cm^{-3}) of "water solution" (which is dilute) in the membrane-matrix, then

$$C_w \cong \frac{t_w \rho_m}{M_w} \quad \text{... (4)}$$

where t_w is the weight-fraction of water in the membrane, and M_w is the molecular weight of water.

Therefore, from equations (3) and (4),

$$J_w \cong -D_w \frac{t_w \rho_M V_w}{RT\, M_w}(\partial_P/\partial x)_M \quad \text{... (5)}$$

Assuming for a dilute solution,

$$\frac{\rho_m V_w}{M_w} \cong 1 \quad \text{... (6)}$$

equation (5) becomes

$$J_w \cong -D_w \frac{t_w}{RT}(\partial_P/\partial x)_M \quad \text{... (7)}$$

On the assumption that the pressure gradient in the membrane is linear, one obtains from equation (7),

$$J_w \cong -D_w \frac{t_w}{RT}(\Delta P/d)_M \quad \text{... (8)}$$

where d is the *effective* thickness of the membrane, and ΔP, the pressure difference across it.

It follows from equation (8),

$$d \cong D_w \frac{t_w}{RT}(\Delta P/J_w)_M \quad \text{... (9)}$$

(Omitting the negative sign, which merely indicates the direction of the flux with respect to the pressure gradient)

From literature[3], some rough estimates of various parameters of equation (9) may be used for the evaluation of d.

$J_w = 18.0 \times 10^{-4}$ g.cm^{-2}. $sec^{-1} = 1.0 \times 10^{-4}$ mol. cm^{-2}. sec^{-1} ;

P = 100 atmosphere (which acts across d, the *effective* thickness of the membrane M) ;

$D_w = 1.0 \times 10^{-6}$ cm^2. sec^{-1} ;
R = 0.082 litre-atmosphere. A^{-1}. mol^{-1} ;
T = 300 A ;

So, one obtains, on these substitutions, from equation (9),

$$d = \frac{1.0 \times 10^{-6}\, t_w \times 1.0 \times 10^{2}}{0.082 \times 10^{3} \times 300 \times 1.0 \times 10^{-4}} \text{ cm}$$

$$\text{or,}\quad d = \frac{t_w}{2.4} \times 10^{-4} \text{ cm}$$

$$= (t_w/2.4) \text{ micron} \quad \text{... (10)}$$

In such membranes, t_w is of the order 0.2, and hence, from equation (10),

$$d \simeq 0.1 \text{ micron},$$

which is in good agreement with the postulated thickness[3] of the dense surface-layer of such membranes.

References

1. R. L. Riley, J. O. Gardner and U. Merten, *Science*, 1964, 143, 801.
2. R. L. Riley, U. Merten and J. O. Gardner, *Desalination*, 1966, 1, 30.
3. H. K. Lonsdale, in "Desalination by Reverse Osmosis", Ed. U. Merten (M. I. T. Press, Cambridge, Mass.), 1966.

Kinetics and Mechanism of Alkaline Hexacyanoferrate(III) Oxidation of Levulinic Acid

BHARAT SINGH*, B.B. SINGH and S. SINGH

Chemical Laboratories, University of Allahabad, Allahabad-211 002

Manuscript received 29 January 1979, revised 15 January 1980, accepted 9 April 1980

THE earlier studies on alkaline hexacyanoferrate(III) oxidation of the organic compounds showed that the anions derived from the organic acids are oxidised by hexacyanoferrate(III) ion[1]. However, Speakman and Waters[2] have suggested complex mechanism for the oxidation of aldehydes, ketones and paraffins. Singh and co-workers[3] suggested that the oxidation of formaldehyde takes place by free radical mechanism. The present study aims at getting more definite information regarding the mechanism of oxidation of levulinic acid by alkaline hexacyanoferrate(III).

Experimental

The sample of levulinic acid was of E. Merck grade and all other chemicals were of G.R. (S. Merck). The rate of oxidation was determined titrimetrically[3].

Stoichoimetry :

The equivalents of hexacyanoferrate(III) required per mole of levulinic acid were found to be four. The acetic and formic acids were identified chromatographically. The stoichiometry of the reaction may be given as

$$CH_3CO(CH_2)_2COOH + 4\overline{O}H + 4Fe(CN)_6^{3-}$$
$$= 4Fe(CN)_6^{4-} + 2CH_3COOH + HCOOH + H_2O$$

* Correspondence to this Author.

Results

The results obtained under different conditions are reported in Table 1. The constant value of pseudo first order rate constant shows that the order with respect to hexacyanoferrate(III) is one. Pseudo first order rate constants obtained at different concentrations of both levulinic acid and hydroxide ion were directly proportional to the concentrations of levulinic acid and hydroxide ion respectively showing thereby first order dependence of the reaction on each levulinic acid and hydroxide ion. This is also confirmed by constant values of $k_1/[\overline{O}H]$ [Substrate] given in the last column of the table. The work has been carried out at three more temperatures and results are given in Table 1. The effect of ionic strength of the medium was also studied and results are given in the table. The energy of activation was found to be 12.1 K cal mol^{-1}.

TABLE 1—EFFECT OF VARYING [REACTANTS] ON REACTION RATE

Temp. °C	$10^3[Fe(CN)_6^{3-}]$ M	10^2[LA] M	$10^2[\overline{O}H]$ M	(μ) M	10^2k_1 min^{-1}	k_2K M^{-2}min^{-1}
35	1.25	2.00	3.20	0.07	0.76	—
35	1.44	2.00	3.20	0.07	0.79	—
35	1.66	2.00	3.20	0.07	0.76	—
35	2.00	2.00	3.20	0.07	0.73	—
35	2.50	2.00	3.20	0.07	0.69	—
35	3.34	2.00	3.20	0.07	0.73	—
35	4.00	2.00	3.20	0.07	0.71	—
35	2.00	2.00	3.20	0.10	1.06	—
35	2.00	2.00	3.20	0.125	1.40	—
35	2.00	2.00	3.20	0.20	2.00	—
35	2.00	2.00	3.20	0.25	2.44	—
35	2.00	2.00	3.20	0.30	2.76	—
35	2.00	0.80	3.20	0.125	0.60	2.30
35	2.00	1.00	3.20	0.125	0.72	2.25
35	2.00	1.25	3.20	0.125	0.96	2.40
35	2.00	1.40	3.20	0.125	1.10	2.45
35	2.00	1.60	3.20	0.125	1.18	2.34
35	2.00	2.00	3.20	0.125	1.58	2.39
35	2.00	3.00	3.20	0.125	2.28	2.37
35	2.00	2.00	2.50	0.125	1.15	2.55
35	2.00	2.00	4.00	0.125	1.90	2.37
35	2.00	2.00	5.00	0.125	2.28	2.28
35	2.00	2.00	6.66	0.125	3.24	2.43
35	2.00	2.00	10.00	0.125	4.86	2.43
30	1.25	2.00	3.20	0.07	0.47	—
40	1.25	2.00	3.20	0.07	1.12	—
45	1.25	2.00	3.20	0.07	1.70	—

LA→Levulinic Acid.

Discussion

In the light of above observations, the probable

scheme of oxidation may be considered as follows :

$$CH_3-\overset{\overset{O}{\|}}{C}(CH_2)_2-CO\bar{O}+O\bar{H} \overset{K}{\rightleftharpoons}$$
(S)

$$CH_3-\overset{\overset{\bar{O}}{|}}{C}=CHCH_2CO\bar{O}+H_2O \quad \text{(I)}$$
($\bar{S}$)

$$\bar{S}+Fe(CN)_6^{3-} \xrightarrow[\text{slow}]{k_2} \text{radical}+Fe(CN)_6^{4-}$$
$$\text{Fast} \downarrow Fe(CN)_6^{3-}$$

$$\text{Final Products} \xleftarrow{\text{fast}} \text{Intermediate Product} \quad \text{(II)}$$

The rate of oxidation could obviously be given by rate of disappearance of hexacyanoferrate(III) as shown in step(II), i.e.,

$$\frac{-d[Fe(CN)_6^{3-}]}{dt}=k_2\,[Fe(CN)_6^{3-}][\bar{S}] \quad (1)$$

The net rate of oxidation of levulinic acid thus can be obtained on substituting the value of [$\bar{S}$] from step (I) in eqn. (1) and is given as

$$\frac{-d[Fe(CN)_6^{3-}]}{dt}=k_2K[S][O\bar{H}][Fe(CN)_6^{3-}] \quad \dots \quad (2)$$

where K is the equilibrium constant and S is substrate anion. At constant [S] and [O$\bar{H}$], k_2K [S] [O$\bar{H}$] can be replaced by pseudo first order rate constant k_1.

The observed first order dependence of the reaction on each hexacyanoferrate(III), levulinic acid and hydroxide ion concentration is obvious from the equation (2). The rate determining step would involve interaction between two negatively charged ions [obvious from step (II)]. For this step a positive salt effect is expected. The effect of ionic strength of the medium on reaction rate was studied by employing different concentrations of potassium chloride (Table 1). Our experimental results are in complete agreement with the above facts.

In most of the oxidation reactions hexacyanoferrate(III) resembles Cu(II) which involves free radical formation and rapidly oxidises it[4-6]. Hexacyanoferrate(III)-hexacyanoferrate(II) system, which has higher redox potential than Cu(II)-Cu(I), substantiates better possibility of the rapid oxidation of the free radical with hexacyanoferrate(III) in the alkaline medium and the rapid oxidation of the free radicals might completely mask the polymerisation. Sometimes the vinyl compounds themselves are oxidised under the experimental conditions used and the test for free radicals fails[7]. Moreover, no spectrophotometric test for complex formation was observed.

References

1. I. R. Wilson, *Rev. Pure. Appl. Chem.*, 1966, 16, 103.
2. P. T Speakman and W. A. Waters, *J. Chem. Soc.*, 1955, 40.
3. V. N. Singh, M. C. Gangwar, B. B. L. Saxena and M. P. Singh, *Canad. J. Chem.*, 1969, 47, 1051.
4. M. P. Singh and S. Ghosh, *Z. Phys. Chem.*, 1956, 204, 1; 1957, 207, 187, 198.
5. K. B. Wiberg and W. G. Nigh, *J. Amer. Chem. Soc.*, 1965, 87, 3849.
6. J. K. Kochi, B. M. Graybill and M. Kwiz, *J. Amer. Chem. Soc*, 1964, 86, 5257.
7. V. N. Singh, M. P. Singh and B. B. L. Saxena, *Indian J. Chem.*, 1970, 8, 522.

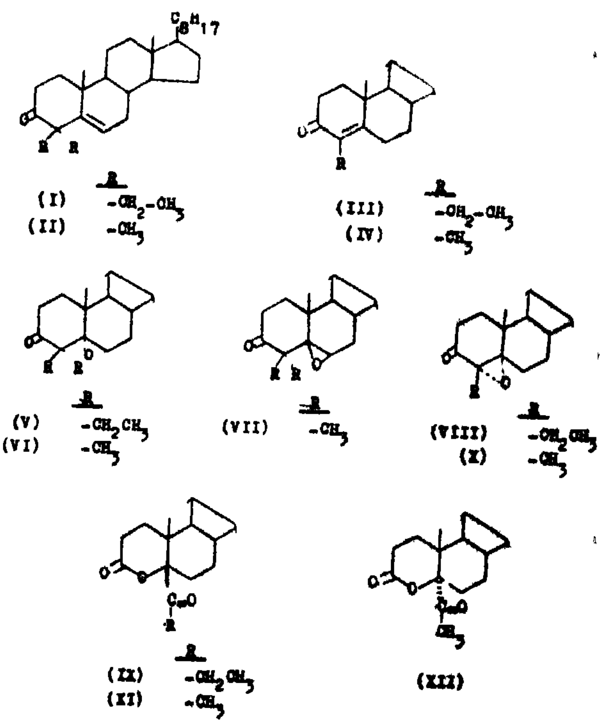
Baeyer-Villiger Oxidation of Steroidal Ketones-V

SHAFIULLAH* and M. A. GHAFFARI

Department of Chemistry, Aligarh Muslim University, Aligarh-202 001, India

Manuscript received 2 February 1979, revised 21 September 1979, accepted 9 April 1980

IN continuation of our reports on Baeyer-Villiger oxidation of steroidal ketones[1-4], we subjected compounds(I-IV) to perbenzoic acid oxidation in the presence of *p*-toluenesulphonic acid, as catalyst. A number of anticipated products were successfully isolated from 4-substituted derivatives of cholest-5-en-3-one(I-II) and cholest-4-en-3-one(III-IV).



Experimental

General Procedure for the oxidation of ketone (I-IV) :

To a solution of ketone (1 g) in chloroform (12 ml) was added a chloroform solution of perbenzoic acid (2.5 moles) and a few crystals of *p*-toluenesulphonic acid. After allowing the reaction mixture to stand at room temperature for a week, the solvent was removed under reduced pressure. The residue was extracted with ether, the ethereal solution was washed with sodium bicarbonate (5%), water and dried over anhydrous sodium sulphate. The solvent was evaporated. The oil (~0.8 g) thus obtained was chromatographed over silica gel (20 g). Elution with pet. ether : ether provided the compounds (Table 1).

TABLE 1

Compounds	Solvent ratio pet. ether : ether	M.P. °C	Yield [%]	Formula	Analysis% C	Found (Calcd.) H
(V)	25 : 1	84	20	$C_{31}H_{52}O_2$	81.70 (81.57)	11.4 (11.4)
(VI)	25 : 1	144	10	$C_{29}H_{48}O_2$	81.61 (81.32)	11.28 (11.21)
(VII)	24 : 1	187	15	—	—	—
(VIII)	20 . 1	96	15	$C_{29}H_{48}O_2$	81.70 (81.32)	10.95 (11.21)
(IX)	18 : 1	112	15	$C_{29}H_{48}O_3$	77.98 (78.40)	10.66 (10.80)
(X)	18 : 1	125	10	$C_{28}H_{46}O_2$	80.80 (81.10)	11.21 (11.20)
(XI)	9 . 1	120	7	$C_{28}H_{46}O_3$	78.20 (78.10)	10.70 (10.80)
(XII)	16 · 1	158	10	—	—	—

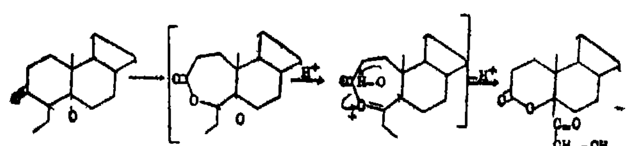
Results and Discussion

The compound (I) on treatment with 2.5 moles of perbenzoic acid (*p*-toluenesulphonic acid in catalytic amount) furnished a product m.p. 84°, $C_{31}H_{52}O_2$. This molecular composition suggests the addition of an oxygen atom to the parent compound (I). The i.r. spectrum of the compound gave bands at 1710 (>C=O) and 875 cm⁻¹ (epoxide). In n.m.r. spectrum* the absence of vinylic proton and presence of doublet at δ 2.91d ($J_{6,7}$ = 5Hz) integrating for one proton, ascribable for C_6-β*H*, account for the formation of 5α, 6-epoxy-4,4-diethyl-5α-cholestan-3-one(V).

The compound (II) under similar conditions provided two isomeric epoxides, m.pts. 144° and 187°, analysed for $C_{29}H_{48}O_2$. In the i.r. spectrum of the compound m.p. 144°, bands were seen at 1710 (>C=O) and 720 cm⁻¹ (epoxide). No band for double bond was observed. In the n.m.r. spectrum the signal observed at δ2.93d ($J_{6,7}$=5Hz) integrating for one proton is assigned for C_6-β*H*

The i.r. spectrum of the compound m.p. 187°, exhibited bands at 1700 (>C=O) and 805 cm⁻¹ (epoxide). The n.m.r. spectrum gave a multiplet at δ3.06 integrating for one proton assignable to C_6-α*H*. On the basis of spectral data the compound m.p. 144° has been assigned the structure as 5, 6α-epoxy-4,4-dimethyl-5α-cholestan-3-one(VI) and compound (VII) m.p. 187° as β-isomer of (VI).

The compound (III) on perbenzoic acid (2.5 moles) oxidation furnished two products of m. pts. 96° and 112°. The compound, m.p. 96°, analysed for $C_{29}H_{48}O_2$ and the i.r. spectrum showed bands at 1700 (>C=O), 790 cm⁻¹ (epoxide). Only methyl signals were observed in the n.m.r. spectrum of the compound. The epoxide has been shown to be an α-oriented on the mechanistic ground[8] as well as from previous observations[6]. Thus the compound m.p. 96° is 4α, 5-epoxy-4β-ethyl-5α-cholestan-3-one (VIII). The i.r. spectrum of the compound (IX), m.p. 112° with molecular composition $C_{29}H_{48}O_3$, exhibited bands at 1700 (>C=O) and 1750 cm⁻¹ (δ-Lactone Carbonyl). The n.m.r. spectrum showed a multiplet centred at δ2.4(4*H*, ascribable to α-methylene protons). The propanyl derivative (IX) may be due to the acid catalysed rearrangement of the intermediate (XIII) (Scheme 1). Such type of intermediate was also suggested by Pinhey and Schaffner[7]. The structure (IX) as 5β-propanyl-4-oxa-5β-cholestan-3-one was further substantiated by conversion of (VIII) to (IX) on treatment with perbenzoic acid under similar conditions.



(VIII) (XIII) (IX)

Scheme—1

The compound (IV) on similar oxidation afforded known compounds (X), m.p. 125°, (XI), m.p. 120° and (XII), m.p. 158° (identical in all respect)[7].

Acknowledgement

We are thankful to CSIR, New Delhi for financial help and Head, Department of Chemistry for providing necessary facilities, to Prof. M. S. Ahmad for useful discussion.

References

1. M. S. AHMAD, A. H. SIDDIQI and SHAFIULLAH, *Indian J. Chem.*, 1970, 8, 786.

* Angular and side chain methyl protons appeared in the compounds described between δ1.0-0.66.

2. M. S. AHMAD, SHAFIULLAH, M. MUSHFIQ and (in part) M. ASIF, *Indian J. Chem.*, 1970, 8, 1062.

3. M. S. AHMAD, SHAFIULLAH and M. MUSHFIQ, *Aust. J. Chem.*, 1974, 27, 2698.

4. SHAFIULLAH and E. AHMAD, Abstract National Academy of Sciences, India, 1978, 10.

5. L. F. FIESER and M. FIESER, Steroid (Reinhold, New York), 1959.

6. S. AKAGI and K. TSUDA, *Chem. Pharm. Bull.* (Tokyo), 1961, 9, 464.

7. J. T. PINHEY and K. SCHAFFNER, *Aust. J. Chem.*, 1968, 21, 1873.

Chemical Investigation of the Leaves of *Phlogacanthus thyrsiflorus*

S. K. BANERJEE, S. BISWAS and M. K. CHOUDHURY

Department of Chemistry, Bose Institute, Calcutta-9

Manuscript received 29 October 1979, accepted 9 April 1980

PHLOGACANTHUS thyrsiflorus[1] (family Acanthaceae) is used medicinally like *Adhatoda vasica* which has been reported to be expectorant and mild bronchial antiseptic[2]. The presant communication reports the isolation of β-sitosterol, lupeol and betulin from the leaves of *P. thyrsiflorus.*

The petroleum ether (b.p. 60-80°) extract of the air-dried leaves of *P. thyrsiflorus* on column chromatography over silica gel furnished three compounds designated as compounds A, B and C.

Compound A : $C_{29}H_{50}O$ (M^+ 414), m.p. 136-37° (EtOH), $[\alpha]_D^{21} -35.6$ ($CHCl_3$), gave a violet to green colour in the Lieberman-Burchard test indicating it to be a phytosterol. On heating with acetic anhydride and pyridine on steam bath it yielded an acetate, $C_{31}H_{52}O_2$ (M^+ 456) m.p. 127-28°, $[\alpha]_D^{21} -41.4°$ ($CHCl_3$). The identity of compound A with β-sitosterol was confirmed by comparison of m.p., m.m.p., optical rotation and TLC with an authentic sample.

Compound B : $C_{30}H_{50}O$ (M^+ 426), m.p. 211-12°. It gave a violet to pink colour in the Lieberman-Burchard test indicating it to be a terpenoid. On heating with acetic anhydride and pyridine on steam bath it yielded a monoacetate, $C_{32}H_{52}O_2$ (M^+ 468), m.p. 213-15°, $[\alpha]_D^{21} +47.7°$ ($CHCl_3$). The identities of compound B and its acetate with lupeol and its acetate respectively were established by comparison (m.p., m.m.p., TLC and IR) with authentic samples.

Compound C : $C_{30}H_{50}O_2$ (M^+ 442), m.p. 258°. It showed violet-pink colour in the Lieberman-Burchard test. Its mass spectral fragmentation pattern was found to be very similar to that of betulin[3]. On heating with acetic anhydride and pyridine on steam bath it furnished a diacetate, $C_{34}H_{54}O_4$ (M^+525) m.p. 221°. Compound C was identified as betulin by comparison of m.p., m.m.p., TLC and IR spectra with an authentic sample of betulin.

Acknowledgement

The authors wish to thank Prof. S. K. Mukherjee, Ex-Director, Prof. A. K. Sen, Head of the Department of Chemistry and Prof. A. K. Barua, Bose Institute, Calcutta, for their interest in the work.

References

1. R. N. CHOPRA, S. L. NAYER and I. C. CHOPRA, "Glossary of Indian Medicinal Plants", CSIR, New Delhi, 1956, p. 190.

2. R. N. CHOPRA, S. L. NAYER and I. C. CHOPRA, "Glossary of Indian Medicinal Plants", CSIR, New Delhi, 1956, p 7.

3. G. R. WALLER, "Biochemical Application of Mass Spectrometry", Wiley-Interscience, 1972, p. 875.

J. Indian Chem. Soc.,
Vol. LVII, June 1980, pp. 666

Book Review

A Text Book of Applied Chemistry for Home Science and Allied Sciences by Thankamma Jacob, published by the Macmillan Company of India Ltd.

The book written in 15 chapters deals with many consumer items used in our daily livnig. Information regarding chemical constitution, uses and abuses, economics, harmful effects etc. of common drugs, cosmetics, pesticides, poisons in food, environmental pollution, fuels, metals, plastics etc. have been neatly summarised in an encyclopedia style. This is a great deal of work considering the wide range of items covered in the book. Mrs. Jacob is a well known personality in the consumer movement in India and wrote two other books in this field earlier, viz. Food adulteration (Macmillan, 1975) and Foods, Drugs and Cosmetics (Macmillan, 1971). The present book covers a much wider area. The author did not intend to present chemistry in detail but she sought to describe consumer items on a 'what is what' basis. The book is thus descriptive in approach. It has been written to meet the requirements and interests of degree students in home science and allied sciences in India. However, consumer with good background in chemistry may find the book useful for a quick information.

I felt that a chapter on food itself projecting our daily requirements of proteins, carbohydrates, fats, vitamins, minerals etc., their sources, cheaper sources of a nutritional diet, the drawbacks of Indian way of cooking, etc. would have been very useful. Similarly in the chapter on common drugs and medicines inclusion of such topics as principles of immunization, antigens, antibodies etc. would have been welcome.

B. M. Mandal